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COMBUSTION PRODUCTS FROM THE INCINERATION OF PLASTICS

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COMBUSTION PRODUCTS FROM THE INCINERATION OF PLASTICS

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FOREWORD

Man and his environment must be protected from the adverse effects of pesticides, radiation, noise and other forms of pollution, and the unwise management of solid waste. Efforts to protect the environment require a focus that recognizes the interplay between the components of our physical environment--air, water, and land. The National Environmental Research Centers provide this multidisciplinary focus through programs engaged in

- studies on the effects of environmental contaminants on man and the biosphere, and
- a search for ways to prevent contamination and to recycle valuable resources.

In an attempt to investigate the problems of solid waste disposal and pollution, this study analyzed combustion products of plastics. Special consideration was given to technical information and incomplete combustion.

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ABSTRACT

Analysis of the combustion products of plastics was undertaken for three reasons: to provide scientists and engineers with information needed to design incinerators in order to maximize their efficiency while minimizing maintainance and pollution, to identify products of incomplete combustion potentially recoverable for their fuel or crude chemical value; and to identify products of incomplete combustion which would be acutely toxic in an accidental fire. Plastics studied were polyvinyl chloride, polysulfone, polyurethanes, polyimide, Lopac^R, Barex^R, phenol formaldehyde, urea formaldehyde, polyethylene, polypropylene, polystyrene, polycarbonate, polyphenylene oxide, polyester, synthetic fabrics (Dacron^R, Orlon^R, **nylon**), and natural products (wood and wool). One-to three-gram **samples** were heated at a controlled rate from 5 to 50 C/min in the presence of a measured flow of air or air plus oxygen. By this method plastics were never completely combusted to carbon dioxide and water, but rather generated large numbers of gaseous and condensed products. Additional gaseous products included straight-chain saturated and unsaturated hydrocarbons through hexane, aromatic hydrocarbons, hydrogen chloride, sulfur dioxide, cyanides, ammonia, and oxides of nitrogen. Liquefied fractions produced by most plastics were complex mixtures of 10 to 50 compounds, including heterocyclic and polycyclic hydrocarbons.

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CONCLUSIONS

The potential hazard from compounds generated on combustion of a plastic depends on the primary structure of the polymer (its atomic composition), the additives used in formulating the plastic, and the conditions under which it is burned. Little is known of the effect of additives, as the present study deals mainly with combustion products of the polymer. Data accumulated to date indicate that three categories of polymers should be considered: those consisting of carbon, hydrogen, and oxygen; nitrogen-containing polymers; and polymers with halogen or sulfur heteroatoms. Plastics composed of only carbon and hydrogen or carbon, hydrogen, and oxygen form carbon dioxide and water when completely combusted. Incomplete combustion results in production of carbon monoxide as the major toxicant, plus gaseous and condensed hydrocarbon products. The condensate has significant fuel or crude chemical value but may be a source of polycyclic hydrocarbon pollution, particularly from aromatic polymers. Plastics containing nitrogen as a heteroatom produce on complete combustion molecular nitrogen and small amounts of oxides of nitrogen, as well as carbon dioxide and water. On incomplete combustion hydrogen cyanide, cyanogen, nitriles and ammonia may form in addition to hydrocarbon gases, presenting a significant health hazard in open burning or an accidental fire. Any liquid condensate formed may be composed of a variety of organic nitrogen compounds as well as hydrocarbons. Nitrogen compounds are more sensitive than other combustion products to changes in combustion conditions. Generally the more incomplete the combustion, the more ammonia and cyanide will form. Plastics containing halogen or sulfur heteroatoms form acid gases such as hydrogen chloride, hydrogen fluoride, and sulfur dioxide on complete combustion in addition to carbon dioxide and water, and can form organic halogen or sulfur compounds on incomplete combustion. These compounds present air pollution, incinerator corrosion, and toxicity problems requiring special techniques to overcome.

RECOMMENDATIONS

There are dozens of different commercial polymers and to each may be added plasticizers, stabilizers, flame retardants, and other chemicals to produce formulated plastics. It is impractical to study the combustion products of each of the thousands of formulations used, and so some generalizations have to be made. Such generalizations can best be made from data on a few representative samples of each class of polymers and each class of additives, and then by studying known formulations to see if any synergistic processes are occuring. It is recommended that studying combustion products of representative polymers and additives individually will give more meaningful and more widely usable results than studying "synthetic rubbish" mixtures formulated in the laboratory or rubbish mixtures with known amounts of plastics added. Either of these methods tends to dilute and mask any specific effects of specific products. Once analytical data are available for a polymer (or plastic) it is possible to extrapolate that data by computer modeling to a wide variety of applications, although synergistic effects are certainly possible. Compiling present analytical data into a single source and filling in where data are inadequate would provide a useful framework for predicting both burning characteristics and toxicity of combustion products of various plastics.

In view of the types of compounds identified in the liquid residues after incomplete combustion of some plastics, we strongly recommend a study be undertaken to determine if plastics can form polycyclic hydrocarbons such as benzpyrene and benzanthracene on combustion, and if formed, whether antipollution devices on incinerators are sufficient to prevent them from entering the atmosphere. Compounds of the same molecular weight as these carcinogens were detected by mass spectrometry in the present study, but deficiencies in reference spectra prohibited positive identification of the compounds found. It would not be surprising to find polycyclic compounds generated in a pyrolysis or combustion process.

Further study on incineration of plastics should emphasize the contribution of additives to combustion products, the composition and economic value of liquid residues produced under pyrolysis conditions, and generation of particulate matter and adsorption of chemicals onto particulates. Study of gaseous products such as hydrocarbons and cyanides, but not acid gases, are of lesser importance in incineration since such compounds are generally broken down on secondary burning. However, these gaseous products may be acutely toxic and are of the utmost importance in open burning or an accidental fire.

INTRODUCTION

There are two basic environmental concerns involving plastics. The first has to do with their disposal, and the second with the toxicity of their products of combustion when burned (either intentionally for disposal or accidentally as in home fires). We began working on the latter problem about 1963 to determine what hazardous products could be evolved in the heating of polymers and plastics, to provide information to those concerned with the health of people exposed to such products in closed or confined spaces.

In 1969 the study was expanded to include all products of combustion, toxic and non-toxic, in order to fill the need for this type of information in the field of solid waste disposal. The amount of solid waste disposed of by burning is continually increasing, and as a result there is interest in designing incinerators to improve their efficiency, to use the heat energy developed, and to do as much as possible to eliminate them as secondary polluters of air and water. It is thus necessary for the designer to know more about the material he is trying to burn. This is especially true of plastics. Plastics currently account for approximately 2 percent of the total packaging solid waste. They are projected to account for 8 percent of the packaging solid waste by 1976 and 2.8 percent of the total solid waste by 1980.[1,2]

There is reason to believe the percentage of plastics in refuse will increase as they continue to become more prevalent in furniture, clothing, automobiles, construction materials, and packaging. For example, Modern Plastics magazine recently speculated that a two-billion pound per year market for acrylonitrile-based plastics could result if plastic bottles now being test-marketed are accepted for only two major brands of soft drinks.[3] Plastics for disposal are received in bulk by many municipal facilities from manufacturers in their area.

Plastics production figures for 1971 (Table 1) have been reported by Modern Plastics.[4] Such figures were used in choosing representative polymers for the study. The proposed goal of this research grant was to examine combustion products of polysulfone, polycarbonate, methyl methacrylate, polystyrene, acrylonitrile-butadiene-styrene, polyethylene and polypropylene. In addition, although information on polyvinyl chloride had already been published, study of this plastic was to be extended to determine products generated at higher temperatures. During the grant period it became apparent that there was greater interest in some plastics not initially chosen for study. Polyurethanes were thus substituted for methyl methacrylate and Lopac[R] and Barex[R] were substituted for acrylonitrile-butadiene-styrene. This selection

TABLE I

PLASTICS PRODUCTION, 1971*

Plastic	Million pounds
Polyethylene (high and low density)	6,400
Polystyrene (including copolymers)	3,840
Polyvinyl chloride (including copolymers)	3,320
Polypropylene	1,260
Phenolic	1,067
Urethane foam	930
Polyester	810
Urea and melamine	679
All non-PVC vinyls	650
Alkyd	610
Coumarone-indene and petroleum resins	360
Cellulosics	165
Miscellaneous	794

*Adapted from The Statistics for 1971, Modern Plastics, 49 (1): 41, January, 1972.

included some of the high-volume plastics as well as newer plastics with good growth potential.

The combustion products of many polymers have been analyzed under vacuum or inert atmosphere, primarily for the purpose of determining polymer structure. Madorsky describes such work done under vacuum on fourteen types of polymers.[5] No comprehensive work has been done, however, on the combustion of these polymers or formulations of them in air. Principle publications are listed in the references. A group at the New York University College of Engineering and Science, under the direction of E. R. Kaiser and A. A. Carotti, studied the effect of plastics on the operation of municipal incinerators in the New York City metropolitan area, under the sponsorship of both the U. S. Department of Health, Education, and Welfare and the Society of the Plastics Industry.[6] Two Environmental Protection Agency-sponsored projects simultaneous to this studied environmental effects of plastics combustion products. The study, "Incineration of Plastics Found in Municipal Wastes", directed by R. W. Heimburg of Syracuse University Corp., used a small model incinerator to generate products to which plants and animals were exposed.[7] Some of the products were identified. A study by Batelle, Columbus Laboratories, "Fireside Metal Wastage in Municipal Incinerators", attempted to determine the mechanisms involved in incinerator corrosion.[8]

This report includes the qualitative and quantitative information on combustion products of those plastics studied by this laboratory. Some overlap, clearly indicated in the text in the polyvinyl chloride and polyphenylene oxide chapters, occurs with work done under a previous grant. Since polyvinyl chloride is the plastic most often of concern in solid waste management, its inclusion seemed mandatory.

METHODOLOGY

Introduction

The basic analytical system for identifying volatile combustion products of plastics was developed before initiation of this grant and has been modified over the years as new techniques were developed and new instrumentation added to the laboratory.[9] The analysis of each polymer or plastic was carried out in three phases:

1. Thermal analysis was used to determine the temperatures at which chemical and physical changes occurred in the sample.
2. The sample was combusted in a small furnace and compounds liberated within temperature ranges determined to be significant by thermal analysis were identified or characterized.
3. The quantities of identified products were determined, either over a single decomposition step or over the entire combustion run.

Thermal Analysis

Differential thermal analysis (DTA). Differential thermal analysis was used to determine the temperatures at which chemical and physical changes took place in a sample. The apparatus used (Figure 1) was a Robert L. Stone KAH unit. It consists of two chambers which are heated at a continuous and identical rate; each chamber contains a fast-response thermocouple, with the two couples connected in series opposition. The sample (200 mg) is placed in one chamber(x), and an inert reference material, such as aluminum oxide, is placed in the other(s). As the chambers are heated, generally at the rate of 5 to 10 C a minute, there is no output of the series couples until either an endothermic or an exothermic reaction takes place in the sample. In the first case, the absorbed heat results in a slightly cooler sample chamber, which is indicated by the differential couple. In the second case, the sample chamber is slightly warmer than the reference, with a resultant reversed polarity in the signal from the differential couple. It will be noted that there are provisions for circulating air at variable rates through each of the chambers. The chambers have a volume of about 0.1 cc, although microchambers are available that handle considerably less. A cylindrical furnace is placed around the chamber housing, and the temperature of the furnace is programmed to rise at a predetermined rate controlled by a temperature programmer. An amplifier is used for increasing the small thermocouple signals to the millivolt level. The record obtained using this apparatus shows the heat absorbed (from an endothermic

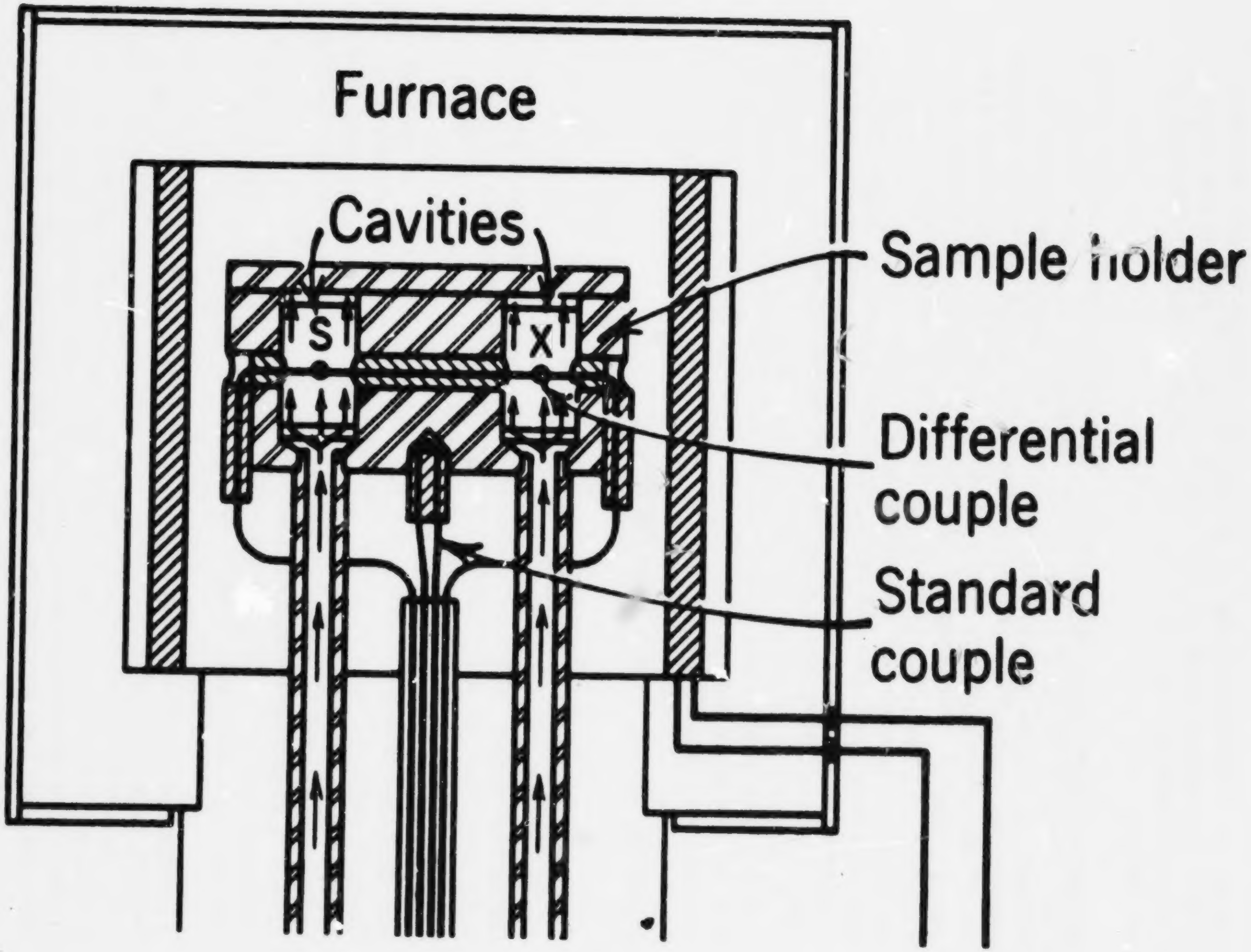


Figure 1. Schematic diagram of a differential thermal analysis (DTA) apparatus

change) or liberated (from an exothermic change) as ΔT, plotted against the temperature of the sample. The ΔT-full-scale sensitivity is from 0.5 to 3.5 C for the various records presented in the text.

Thermogravimetric analysis (TGA). Thermogravimetric analysis provided a record of weight change of the sample as it was heated. Inasmuch as the DTA equipment contained the basic components (a temperature controller and programmer) for a TGA unit, the remainder of the apparatus was built at the University of Michigan following a design developed at Dow Chemical Company by Cobler and Miller.[10] It consists (Figure 2) of a small cylindrical furnace containing a sample pan suspended on a quartz spring. In both this apparatus and the DTA unit, the sample area is a gastight chamber with complete control over the amount of entering air or other gas and means for collecting all emerging gases. The sample is heated at a rate of 3 to 10 C per minute, and its temperature is recorded on the X-axis of an X-Y recorder. The displacement of the platinum pan holding the sample, as measured by the differential transformer below the quartz spring, is recorded on the Y-axis. The final record is then a plot of percent weight remaining versus sample temperature.

Sample Combustion

Combustion gases could be quantitatively collected from the TGA apparatus, but it was found that larger quantities than were available from this unit were desirable or essential. A combustion furnace (Figure 3) with controlled temperature and air supply was designed and built to carry out the combustion on as much as a tenfold scale (2 g) but under the same conditions as in the TGA apparatus. Samples (0.5-2 g) for qualitative and quantitative analysis were placed in porcelain boats in the Vycor^{R} gastight furnace core. A measured amount of purified tank air was swept through the core and collected, along with volatile products, in a Saran^{R} bag so that the total sample volume was usually 2 to 15 liters.

Air supplies were determined for each plastic by calculating the amount necessary to completely convert all the carbon to carbon dioxide when integrated over the entire combustion run, and using an amount less than, roughly equal to, and more than that calculated. The amount calculated was, of course, a deficient supply because all the air passing through the tube was not in the vicinity of the sample and thus available for reaction, and the reaction would only occur with reasonable efficiency at the high end of the temperature range.

The furnace was controlled by a West SCR Stepless Controller. The sample was heated rapidly from room temperature to a temperature

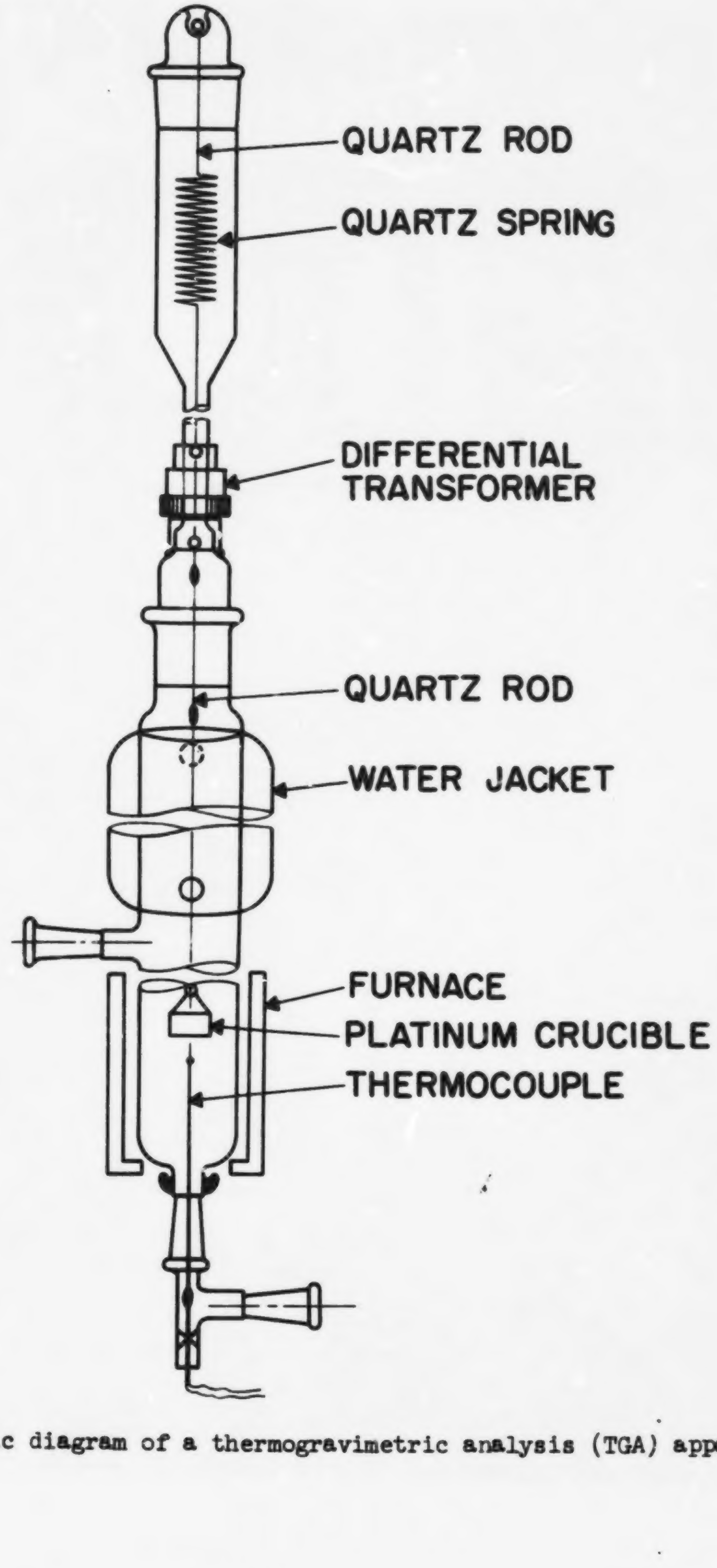


Figure 2. Schematic diagram of a thermogravimetric analysis (TGA) apparatus

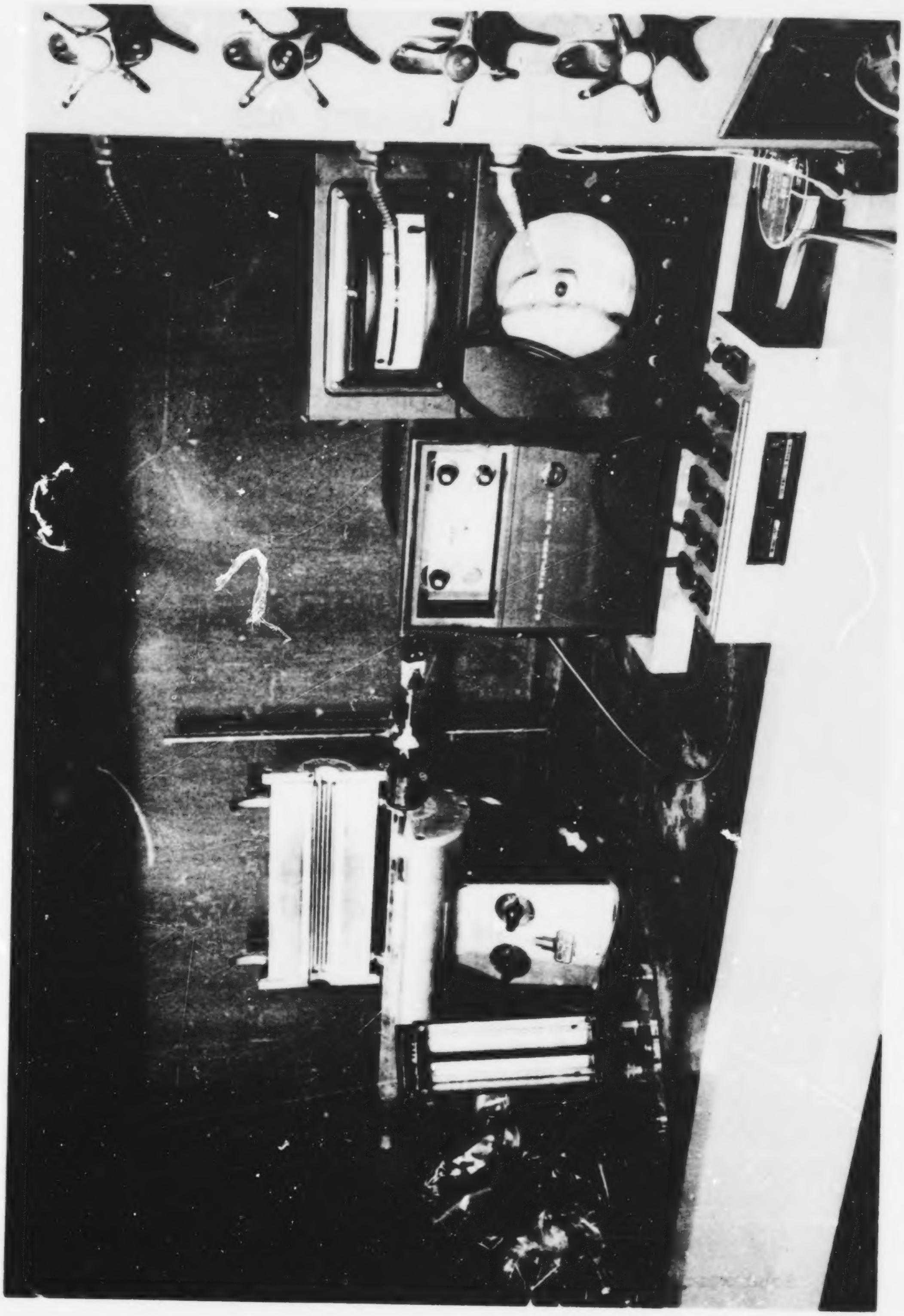


Figure 3. Combustion furnace and temperature control equipment

50 to 100 C below its decomposition temperature and then heated at 5 to 50 C per minute. Initially the upper temperature limit of the apparatus was 800 C, but this temperature was not sufficient to combust some of the newer high-temperature polymers in a reasonable length of time. Thus the limit was changed to 1000 C. Products formed were swept out of the heating zone rather quickly by the continuous air flow, minimizing secondary reactions. Higher-boiling combustion products were thus not broken down further and condensed as liquid residue in either the cool end of the combustion tube or the sample bag.

We believe our method of combusting the samples is realistic when compared with the situation in a fire or incinerator for these reasons: In most fires and in incinerators, the plastic is not normally in an open flame, or if so, only toward the end of its combustion process. For example, in a structural fire, the flame will progress or spread toward the plastic (floor covering), so that it is gradually heated before being exposed to the flame, and then only if the flame proceeds that far. Likewise, in most incinerators the feed mechanism is such that the refuse is gradually carried toward the flame (by conveyer or feed screw) at a rate that makes for slow heating before reaching the flame to avoid cooling the flame. In this case, of course, many of the combustion products that we show will break down further into their combustion products when they reach the flame, but one can frequently predict which of these will do so.

Qualitative Analysis

Major combustion products, present in quantities ranging from 0.1 to 15 percent, were identified directly by infrared spectroscopy. Minor combustion products were identified by mass spectrometry after concentration and separation from the mixture.

Infrared spectroscopy. Combustion gas directly from the sample bag was analyzed by infrared spectroscopy on a Perkin-Elmer 221, in either a 10-cm path-length gas cell or a long-path (up to 40 meters) gas cell. Each compound has a characteristic pattern of infrared absorption bands, allowing major components (>1000 ppm) of the sample to be easily identified. This procedure of direct infrared analysis was, however, not applicable to the minor compounds of the combustion products for two reasons: (a) the large number of lesser components would produce additive, overlapping spectra, which would be impossible to resolve, and (b) the volume of each component is insufficient for the practical application of the long-path gas cell, normally used for the identification of a component present in low concentration.

Gas chromatography. To separate minor components for the purpose of identification, the gas chromatographic technique was used. Gas chromatography involves a column packed with liquid-coated solid support or active solid through which helium or other inert gas is continuously flowing. When a sample is injected, it is swept along by the helium; but components of the sample have different affinities for the liquid coating or active solid and so are absorbed and desorbed at different rates. Thus, they take different times to pass through the column, resulting in a separation. The column is kept in an oven and the temperature can be constant or programmed at any desired rate to elute compounds in a reasonable length of time. A detecting device is located at the end of the column to measure each component as it appears, the output of the detector being recorded. The retention time of a compound on the column is the only clue to its identification, and exact reproducibility of retention times is difficult for a sample producing a large number of closely-spaced peaks. Thus gas chromatography is a good separation technique but a poor identification technique.

Several gas chromatographs were used throughout the study:

Research Specialties with argon ionization detector

Beckman GC-2A with hydrogen flame and thermal conductivity detectors

Wilkens Model H600-B with hydrogen flame and electron capture detectors

Microtek MT 220 with hydrogen flame detectors

Carle Basic Model 9000 with hydrogen flame detectors

Sample concentration. Samples were collected for identification using the MT 220 chromatograph which has dual columns and detectors. To prevent sample destruction by the detector, one column has a stream splitter which allows 10 percent of the eluted gas to go to the detector and 90 percent to emerge at a side arm for collection. Concentration compensated for the reduced amount of sample being detected and also reduced the number of times an individual peak had to be collected before sufficient sample was available for identification. A tenfold concentration was accomplished by passing the combustion gas through a U-tube immersed in Methyl Cellosolve^R-dry ice (-50 C) and then vaporizing the frozen products by heating the U-tube and sweeping it with a small volume of air, so that the total sample volume range was reduced from 2000 to 5000 cc to 200 to 500 cc.

Mass spectrometry. Many of the minor combustion products were identified by mass spectrometry. Figure 4 shows a very general diagram of a mass spectrometer system. The sample is introduced into the source via an inlet system (gas or solid probe, reservoir,

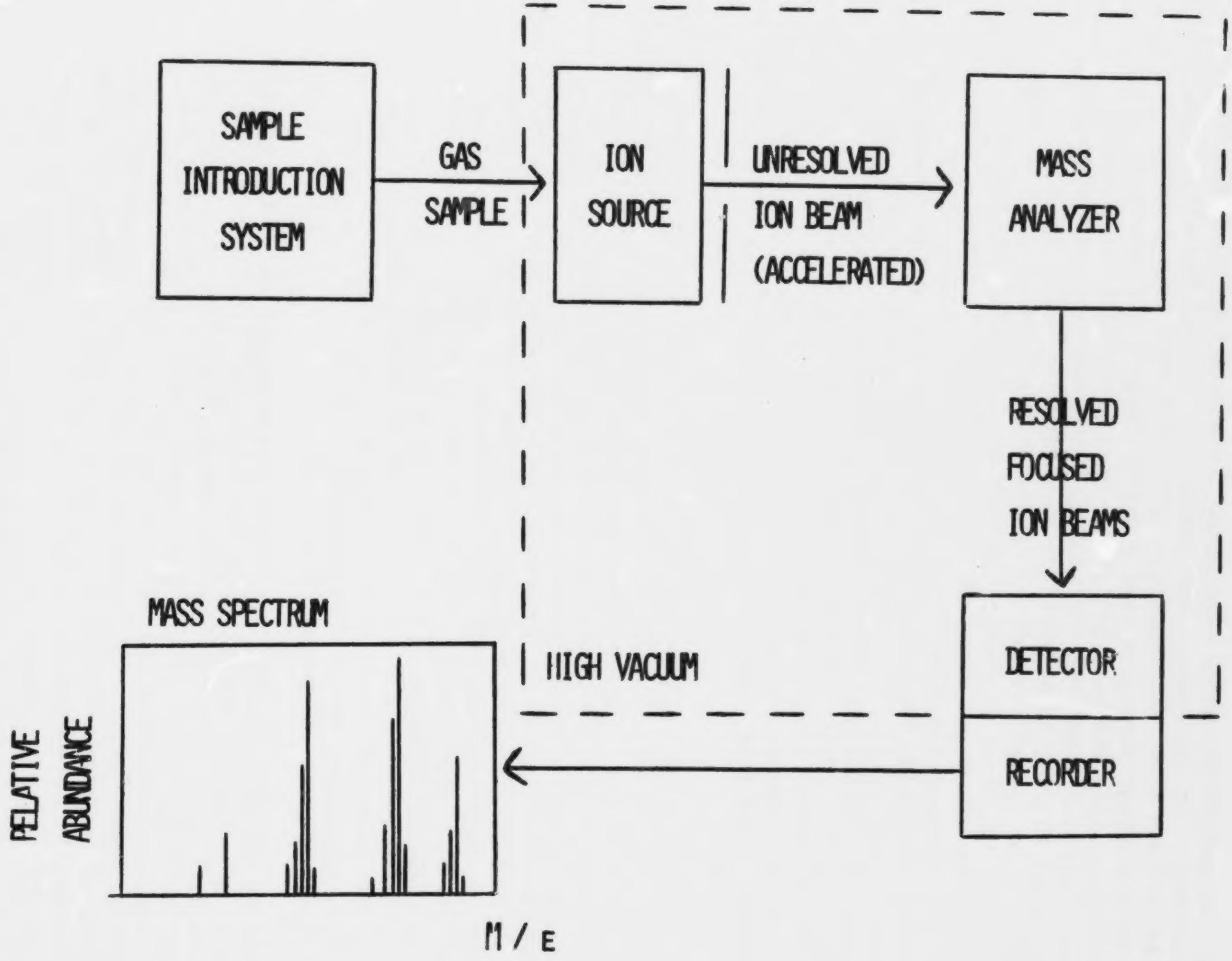


Figure 4. Mass spectrometer system (Adapted from Roboz, J. Introduction to mass spectrometry. New York. Interscience. 1968. p. 10)

gas chromatograph) which also serves to volatilize the sample if necessary. In the source, the sample gas is bombarded with electrons to form ions. The positive ions are formed into a narrow beam by passage through a slit and accelerated by a potential difference into the mass analyzer. Here a magnetic field causes the single ion beam from the source, which contains ions of many different masses, to be resolved into many ion beams, each of these beams containing ions of essentially one mass. Each of these resolved ion beams is focused in turn on a detector and the response amplified and recorded. A mass spectrum is simply a plot of the relative abundance of an ion versus its mass-to-charge ratio. The thing that makes mass spectrometry a useful analytical tool is that for a given energy of bombarding electrons the same fragmentation pattern always results, providing a fingerprint of the compound. Mass spectrometry which is much more sensitive than infrared spectroscopy, can detect nanogram quantities of sample. Since mass spectra of various components of a sample are additive, however, only pure compounds or simple mixtures can be successfully analyzed.

Most of the work was carried out using an AEI MS10 mass spectrometer (Figure 5) with a glass reservoir inlet system. Samples for analysis by mass spectrometry were collected in the following way: effluent which was not sent to the detector emerged from the GC column through a two-way valve and was diverted into a U-tube, filled with glass beads and cooled with liquid nitrogen, in order to condense out everything but the helium carrier gas. The U-tube and its cooling flask were then transferred to the inlet system of the mass spectrometer, the helium was pumped out, and the cooling flask was removed to allow the sample to expand into the reservoir inlet. This inlet could not be heated, thus limiting the analyses that could be performed to compounds boiling below about 130 C, or "volatile" compounds. The MS10 mass analyzer limited analyses to compounds with molecular weights less than 125.

During the last year of this grant period an AEI MS30 double beam mass spectrometer was added to the laboratory (Figure 6), greatly increasing the mass spectrometry capabilities. It included a gas chromatograph inlet so that the sample could be injected onto a chromatograph column and mass spectra of the eluted compounds taken sequentially. The heated inlet and source allowed for analysis of compounds boiling up to 350 C. Liquid residues left after incomplete combustion could thus be studied.

Quantitative Analysis

Infrared spectroscopy and gas chromatography are excellent tools for quantitative analysis. For a well-resolved band in the infrared region, a plot of absorbance versus concentration for a series

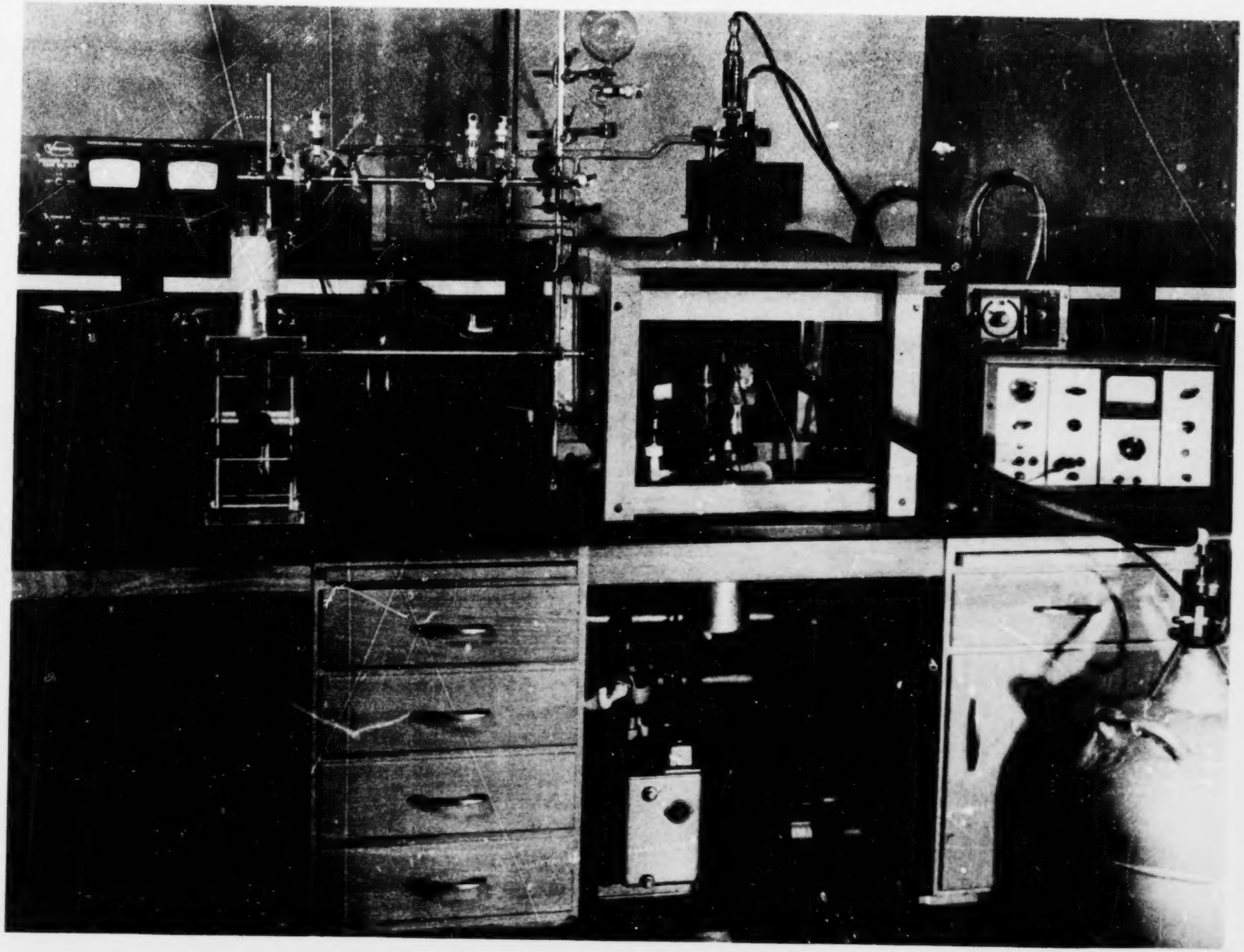


Figure 5. AEI MS10 mass spectrometer with glass reservoir inlet

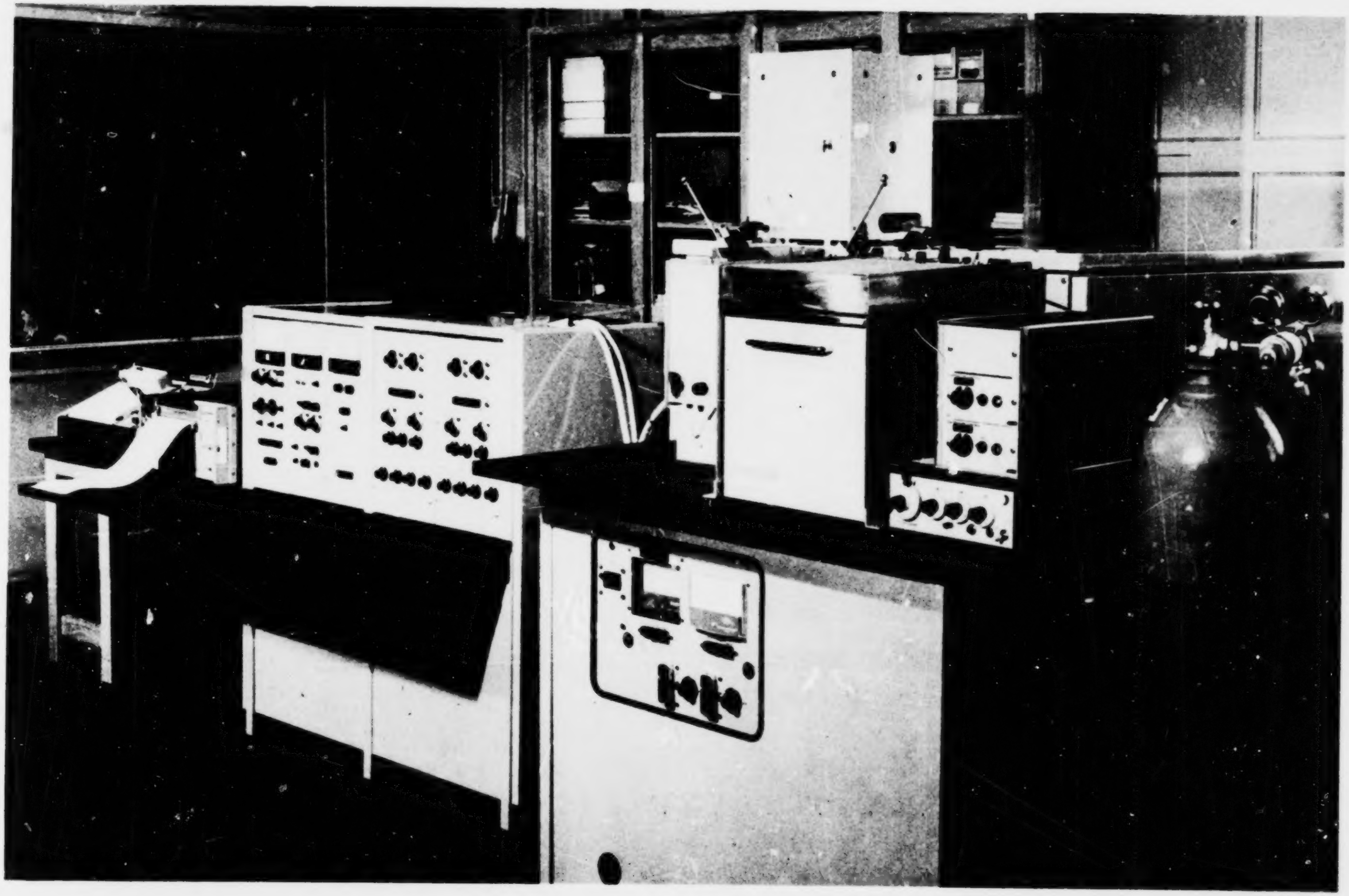


Figure 6. AEI MS30 mass spectrometer with gas chromatograph, probe, and heated reservoir inlets

of standards should yield a straight-line calibration curve. Likewise peak area (or peak height for a symmetrical, well-resolved peak) is proportional to concentration in chromatography allowing calibration curves of peak area (or height) versus concentration to be made from a series of standards. Standards were prepared in either a 20-liter glass carboy with mechanical stirrer or in a Saran^R bag containing a measured volume of air by injecting known quantities of pure liquids or lecture-bottle gases.

A few compounds could not be quantitated by either infrared spectroscopy or gas chromatography. Oxides of nitrogen were quantitated using the Saltzman method[11] and sulfur dioxide was quantitated by a recently-reported ultraviolet method.[12] Hydrogen cyanide and ammonia were quantitated using Orion specific ion electrodes and an Orion Model 801 digital pH meter.

Quantitative analysis of major products in some of the liquid residues produced on combustion of many plastics was unsuccessful. Weighing the combustion tube and bag or washing out the residue with solvent proved exceedingly inaccurate; so the amount of residue was determined by difference from volatile products.

Many tables of numbers are presented throughout the text and some comment on their significance is in order. The analytical experimental error due to such things as sample injection, standard preparation, and peak measurement should be less than ±10 percent. Another potential source of error was introduced by the method of sample collection. Gaseous products came into contact with Saran^R (polyvinylidine chloride) collection bags and Tygon^R tubing. Both materials were found to be inert to small concentrations of hydrocarbon materials over the short period of time (less than two hours) between sample collection and analysis. Ammonia, and possibly other nitrogen products, reacted slowly with Saran^R. Use of Teflon^R bags was considered but was prohibitively expensive. Condensation of higher-boiling products (>100 C) on the large surface area of the bag was minimized by rapid sample analysis.

The rather random nature of the combustion process provided the largest source of experimental deviation. The goal of the study, largely accomplished, was to obtain values reproducible under our combustion conditions to within ±25 percent. However, occasional deviations of ±200 percent or more were observed, using identical combustion conditions. Deviations this large were almost certainly due to ignition of the plastic or its products in the heating zone. Such deviations were largest for carbon dioxide, carbon monoxide, and methane, the products of most complete combustion.

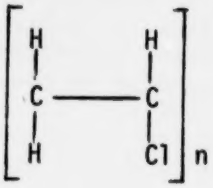
When comparing the data for carbon monoxide when burned with varying amounts of air, it will be noted on some polymers, that more of the compound is formed with increased amounts of air, contrary to what one usually expects. As pointed out earlier, we calculated the amount of air necessary, when integrated over the entire combustion run, to completely convert all the carbon to carbon dioxide. The air supplies used were then less than, roughly equal to, or more than that calculated. However, the amount calculated was a deficient supply because all the air passing through the tube was not in the vicinity of the sample and thus available for reaction. The reaction would only occur with reasonable efficiency at the high end of the temperature range. This, coupled with the possibility that some polymers are inclined to ignite in the heating zone when the amount of air is increased, may result in a greater reduction of the hydrocarbons to carbon without sufficient oxygen to convert it to carbon dioxide.

POLYVINYL CHLORIDE

Introduction

Polyvinyl chloride (PVC), of all the polymers, has been implicated as causing the most serious solid waste disposal problem because of its large volume usage in packaging and its release of hydrogen chloride gas on burning. The potential of this hydrogen chloride to corrode municipal incinerators has long been realized, and has resulted in several states introducing legislation to ban PVC packaging, for example, Michigan House Bill No. 5486.[13]

Polyvinyl chloride has the following structure:



$$\left[-\mathrm{CH_2}-\mathrm{CHCl}- \right]_n$$

Its chemical composition is 38.44 percent carbon, 4.84 percent hydrogen and 56.73 percent chlorine. Low-boiling (<130 C) combustion products of PVC have been studied prior to initiation of this grant, and a summary of results is included.[14] Previous workers concerned with the combustion of vinyl chloride polymers examined them primarily to determine the amounts of hydrogen chloride, carbon dioxide, carbon monoxide, and other major products given off.[15-18] Toxicity to rats of combustion products of the same polymers used in this study has been reported.[19]

Recently concern has been expressed over possible generation of benzyl chloride on cutting PVC film with a hot wire. Since this compound is quite toxic and might be liberated in any inefficient PVC combustion (municipal incineration, home incineration, open burning) its generation was specifically studied, particularly at low temperatures (<350 C) as benzyl chloride decomposes at higher temperatures.

Samples

Four PVC polymers and three formulations of three of the polymers were analyzed under previous grants and are listed as follows:[20] polymers A, B, and C, polyvinyl chloride homopolymers; polymer D, an 85:15 copolymer of vinyl chloride and vinyl acetate; plastic E, a common wire insulation formulation containing 57 percent polymer C; plastic F, a floor tile formulation containing 35 percent copolymer D; and plastic G, a wire insulation formulation containing 51 percent polymer B. Five commercial meat-wrap films (A,B,C,D,E) were tested for benzyl chloride production under the present grant.

Results

Thermal analysis. Differential thermal analysis of polymer C heated at 10 C/min in excess air (Figure 7) shows a dehydrochlorination endotherm at about 310 C, partly obscured by much larger exothermic peaks which begin at 260 C and continue to 600 C, at which temperature the sample is completely combusted. Thermogravimetric analysis of the same polymer heated at 3 C/min in air (Figure 8) shows the weight loss appears to take place in five stages. First is a rapid 60-percent loss up to 280 C corresponding to the DTA endotherm; second, a decreasing rate of loss up to 350 C; third, a slow constant rate of loss to 430 C; fourth, a more rapid rate of loss to 510 C; and finally, a faster rate of loss, for the remainder of the sample. These temperature ranges are used later (Table 4) in describing the change in composition of combustion products with temperature. DTA and TGA records for the other polymers and plastics showed similar steps with ±20-C variations in the temperatures. Thermal analysis was not carried out on the film samples.

Qualitative analysis. This study was primarily concerned with "volatile" products of combustion, or those compounds boiling up to about 150 C. Analysis of the combustion gas by infrared spectroscopy showed absorption bands of hydrogen chloride, carbon dioxide, carbon monoxide, and benzene, along with other bands in the 3000 cm^{-1} region indicating the presence of compounds containing C-H groups. Identification of these other compounds was carried out by separating them from the mixture by gas chromatography and collecting them in individual quantities for identification by mass spectrometry using an AEI MS10. A six-foot-long, 1/4-in.-diameter column of Porapak Q was used to separate compounds boiling at temperatures less than 0 C. Higher-boiling compounds were separated on a 12-foot-long, 1/4-in.-diameter column of 5 percent Squalane on Chromosorb P. Columns were temperature-programmed at 10 C/min to 110 C after an initial period of 5 to 15 minutes at 25 C.

Shown in Figures 9 and 10 are the 51 chromatographic peaks eluted on these two columns representing a minimum of 59 volatile products of combustion (some peaks represent more than one compound) including the three identified by direct infrared analysis. Of this minimum figure of 59, 52 compounds have been identified including carbon dioxide, carbon monoxide, hydrogen chloride and the 49 listed in Table 2.

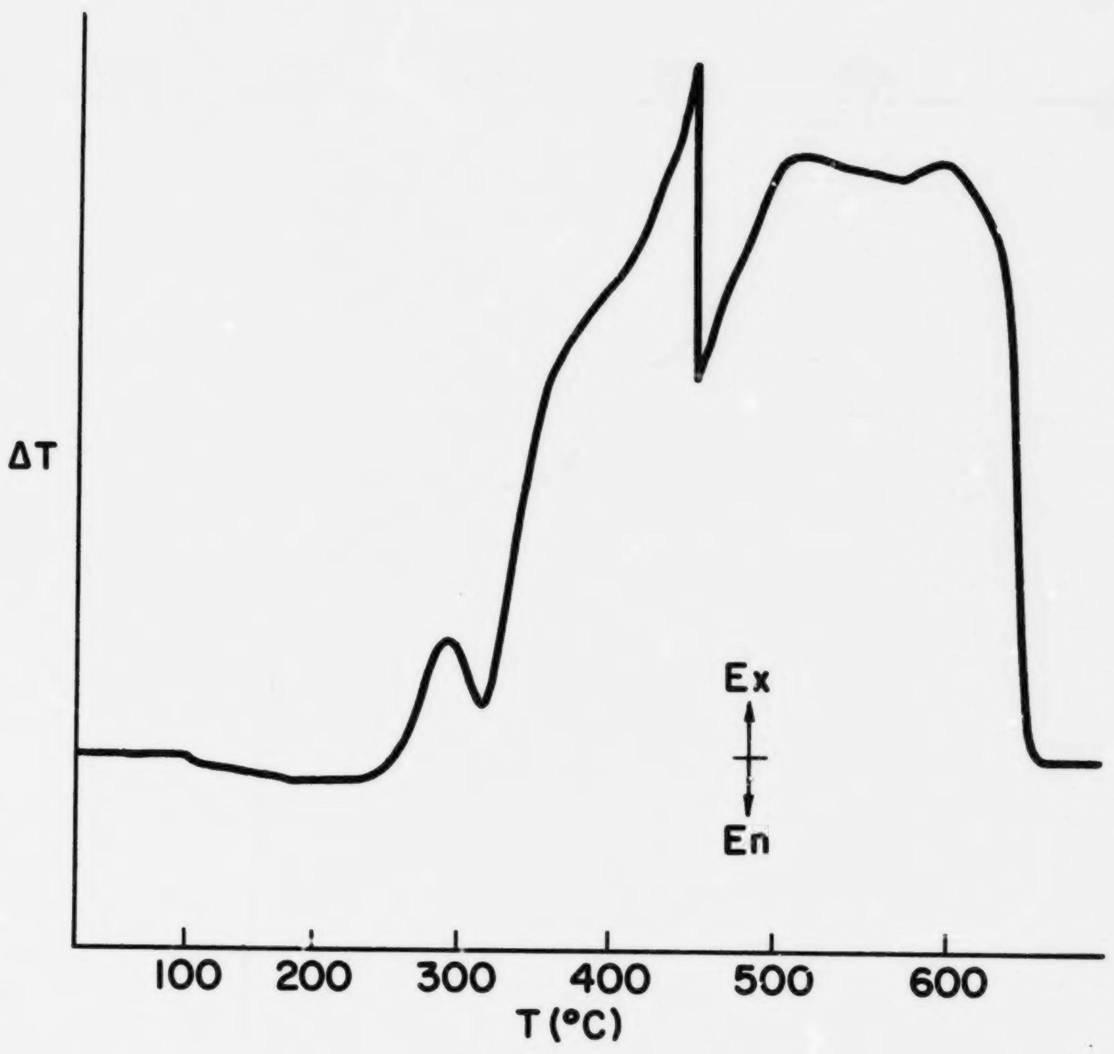


Figure 7. Differential thermal analysis record of polymer C heated at 10 C/min in air

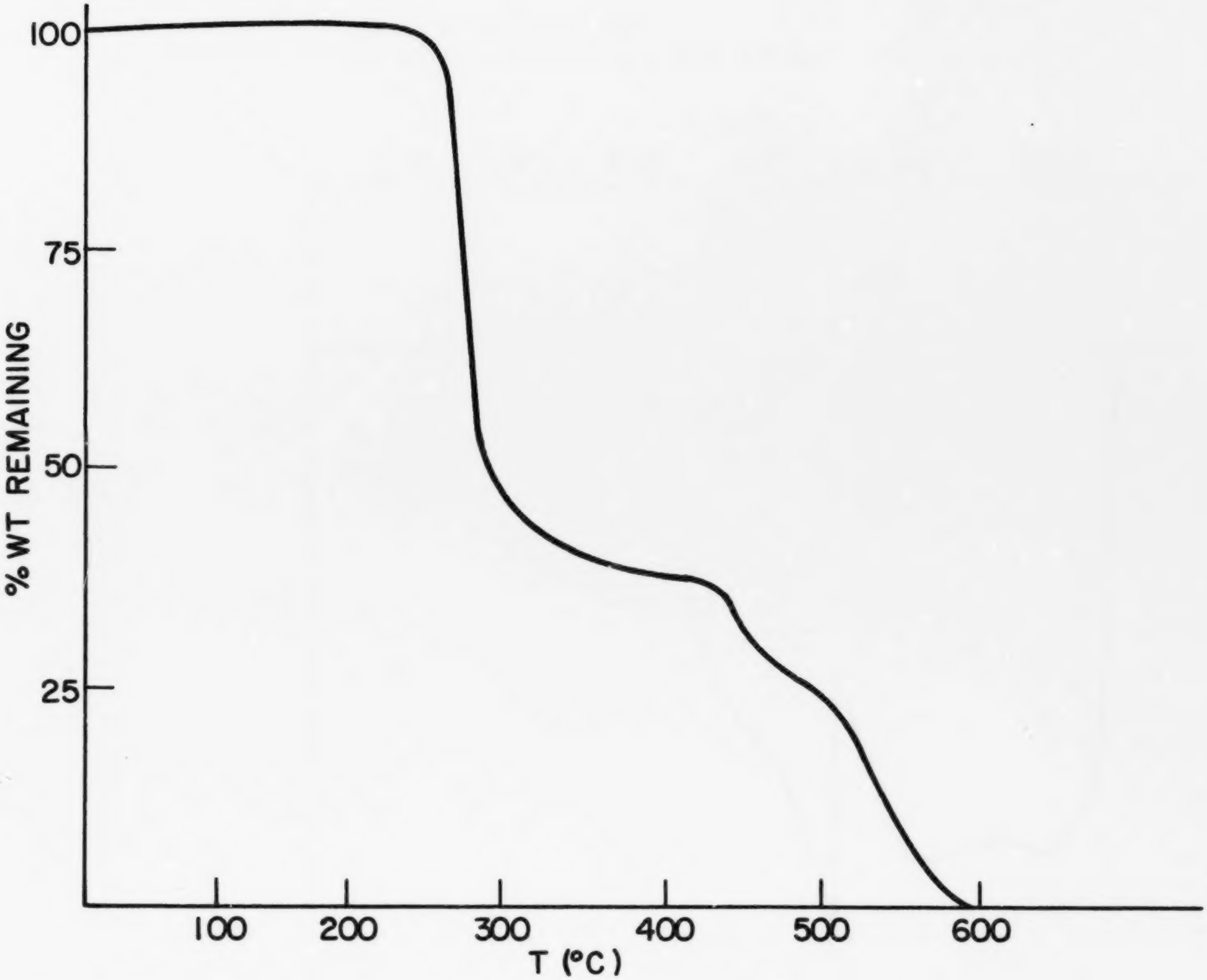


Figure 8. Thermogravimetric analysis record of polymer C heated at 3 C/min in air

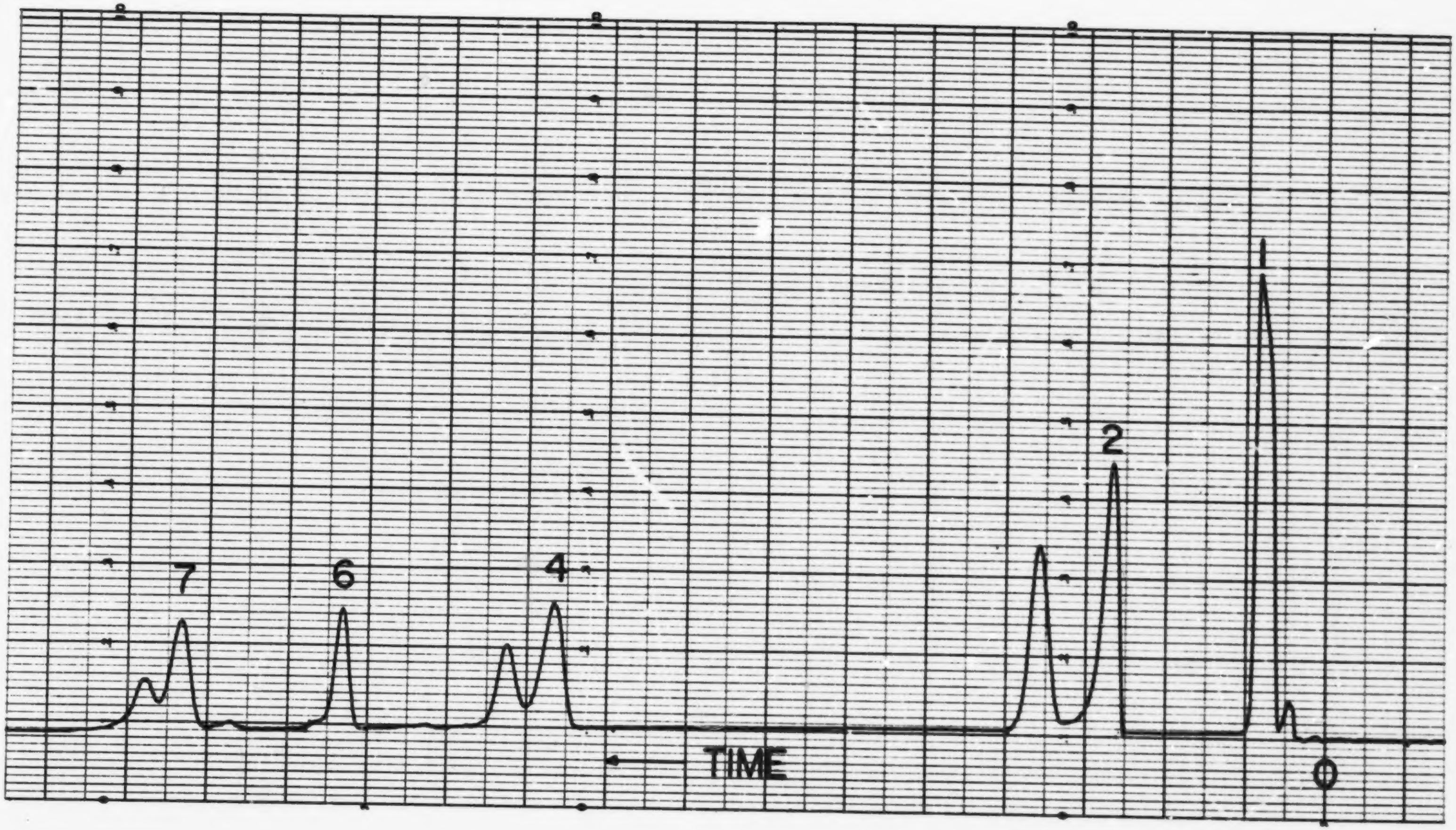


Figure 9. Chromatogram of low-boiling combustion products of polymer A on a Porapak Q column

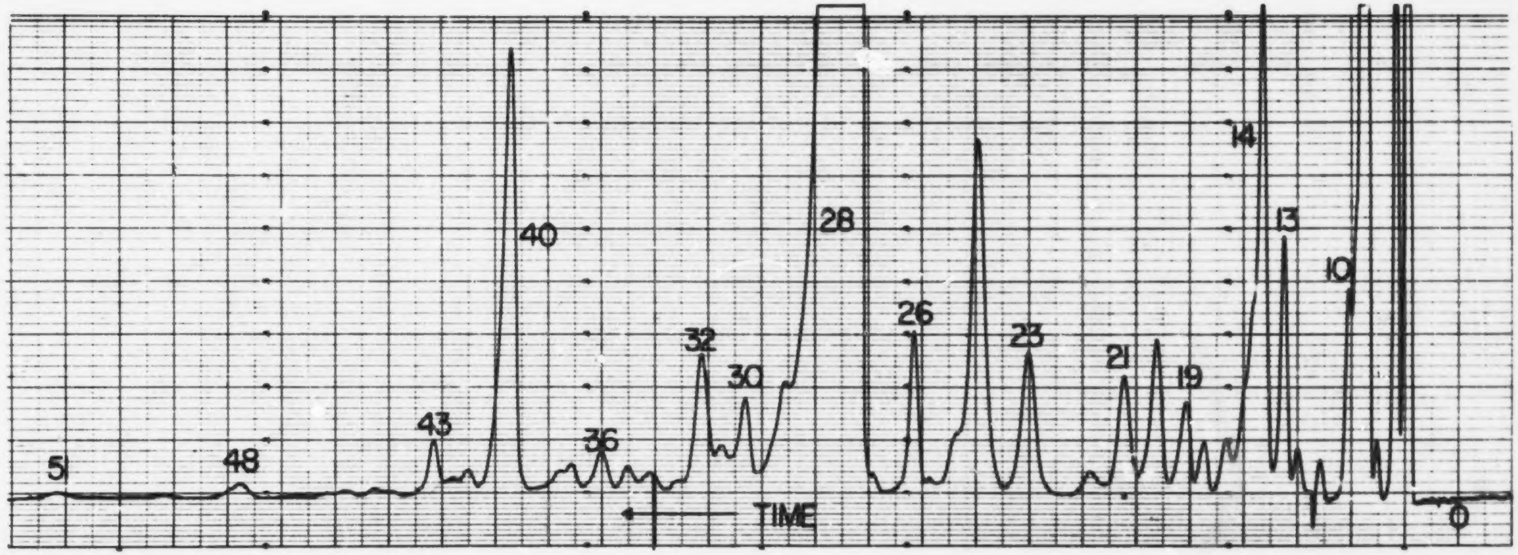


Figure 10. Chromatogram of combustion products of polymer A on a column of 5 percent squalane on Chromosorb P

TABLE 2
IDENTIFICATION OF POLYVINYL CHLORIDE CHROMATOGRAM PEAKS

Peak no.	Identification
1	Methane
2	Ethylene
3	Ethane
4	Propylene
5	Propane, Methyl chloride
6	Vinyl chloride
7	1-Butene, Isobutane, Butadiene
8	Butane
9,10	trans-2-Butene, cis-2-Butene
11	3-Methyl-1-butene
12	Isopentane, 1,4-Pentadiene
13	1-Pentene
14	Pentane
15,16	trans-2-Pentene, cis-2-Pentene
17	2-Methyl-2-butene
18	cis or trans-1,3-Pentadiene
19	cis or trans-2-Penten-4-yne
20	Cyclopentene
21	Cyclopentane
22	2-Methylpentane
23	1-Hexene, 3-Methylpentane
24	Hexane
25	2-Hexene
26	Methylcyclopentane
27	1-Methylcyclopentene
28	Benzene
29	Cyclohexane
30	1-Heptene
31	1,4-Dimethylcyclopentene*
32	Heptane
33	Unidentified
34	3-Ethylcyclopentene
35	Methylcyclohexane
36	Ethylcyclopentane
37	1,2-Dimethylcyclopentene
38	1-or 4-Ethylcyclopentene
39	1-Methylcyclohexene
40	Toluene
41,42	Unidentified
43	Octane
44-47	Unidentified
48	Ethylbenzene
49-51	o-, m-, p-Xylene

*Tentative

Quantitative analysis. All quantitative work was done on the 22 compounds present in the greatest quantities. As a uniform condition for comparing polymers and formulations, the following combustion conditions were adopted: The air supply was 60 cc/min which, when integrated over the entire run, would result in about twice the amount of oxygen necessary to convert all the carbon to carbon dioxide. The plastics were heated (after an initial heating from room temperature) from 200 C to 600 C at a rate of 3 C/min.

Hydrogen chloride was quantitated by infrared spectroscopy, acid-base titration, and silver nitrate titration, and in the case of all the homopolymers amounted to about 580 milligrams per gram. Thus, HCl formed nearly quantitatively from the chlorine atoms of PVC.

A comparison of the combustion products of the three plastics with the combustion products of their polymers is given on Table 3. Except for aromatic compounds, the hydrocarbons in plastics G and E have all increased in quantity over polymers B and C by factors ranging from 1.3 to 8 times. Likewise, the amount of vinyl chloride appears to be about 5 times as great in these samples. Most of the increases are attributable to the breakdown of the phthalate plasticizer, which forms a series of hydrocarbons similar to those produced by PVC. The plasticizer, either dioctyl phthalate of diisodecyl phthalate, cannot be directly responsible for the apparent increase in vinyl chloride.

Different results are noted for plastic F, the floor tile formulation made from copolymer D. This product contains about one third copolymer D, but the hydrocarbon products generated, especially saturated aliphatics and benzene, are considerably less than one third the amount generated by copolymer D. Likewise, the amounts of acetic acid and HCl are less than the 33 percent expected. This product contains about 70 percent inert material, such as asbestos and calcium carbonate, which may play a part in inhibiting breakdown of the polymer and production of hydrocarbons.

The variations in quantities of combustion products of a representative PVC homopolymer as a function of temperature are shown in Table 4. Products were collected in five fractions, selected on the basis of TGA curve inflections, during a single heating run. During the first temperature fraction almost 80 percent of the benzene is formed along with a small amount of toluene and some unsaturated hydrocarbons. Production of hydrogen chloride as determined by analysis of the TGA effluent roughly parallels that of benzene. In the second fraction (280-350 C), carbon dioxide and carbon monoxide appear, toluene continues to increase, but hydrogen chloride and benzene are already decreasing and continue to decrease through the higher ranges. Hydrogen chloride is present

TABLE 3

COMPARISON OF COMBUSTION PRODUCTS OF THE PLASTICS WITH THE COMBUSTION PRODUCTS OF THEIR POLYMERS

Compound	Polymer B	Plastic G	Polymer C	Plastic E	Copolymer D	Plastic F
Hydrochloric acid*	583.	273.	584.	333.	500.	73.
Acetic acid	----	----	----	----	96.	20.
Carbon dioxide	729.	616.	730.	1182.	923.	456.
Carbon monoxide	442.	67.	403.	90.	292.	31.
Methane	4.6	6.6	5.8	6.8	4.4	0.30
Ethylene	0.58	2.3	0.33	2.0	0.60	0.13
Ethane	2.2	3.0	2.5	2.9	2.3	0.13
Propylene	0.47	2.0	0.56	1.4	0.56	0.11
Propane	0.84	1.7	1.1	1.4	0.88	0.10
Vinyl chloride	0.60	3.3	0.52	2.6	0.72	0.30
1-Butene	0.18	1.1	0.28	0.58	0.22	0.06
Butane	0.28	1.1	0.39	0.74	0.29	0.05
Isopentane	0.02	0.15	0.02	0.04	0.02	0.01
1-Pentene	0.06	0.35	0.11	0.15	0.09	0.01
Pentane	0.16	0.58	0.27	0.38	0.21	0.02
Cyclopentene	0.05	0.14	0.58	0.07	0.05	0.004
Cyclopentane	0.05	0.16	0.07	0.09	0.06	0.003
1-Hexene	0.05	0.24	0.09	0.18	0.08	0.01
Hexane	0.12	0.49	0.25	0.35	0.17	0.01
Methylcyclopentane	0.14	0.14	0.07	0.09	0.05	----
Benzene	36.	10.	29.	11.	28.	0.86
Toluene	1.3	0.94	1.1	1.0	0.96	0.04
Residue (inorganic)	----	159.	----	61.	----	709.

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 4

VARIATION OF COMBUSTION PRODUCTS OF POLYMER A WITH TEMPERATURE

Compound	25- 280 C	280- 350 C	350- 430 C	430- 510 C	510- 580 C
Carbon dioxide*	----	9.7	181.	244.	237.
Carbon monoxide	----	20.	46.	151.	181.
Methane	----	0.20	1.3	1.8	0.31
Ethylene	0.04	0.33	0.39	----	----
Ethane	----	0.12	0.94	0.41	----
Propylene	0.06	0.11	0.31	----	----
Propane	----	0.08	0.44	0.11	----
Vinyl chloride	0.04	0.25	0.17	0.02	----
1-Butene	0.02	0.04	0.08	----	----
Butane	----	0.03	0.20	0.02	----
Isopentane	----	----	0.005	0.001	----
1-Pentene	----	0.01	0.03	----	----
Pentane	----	0.01	0.08	0.01	----
Cyclopentene	----	0.02	0.01	----	----
Cyclopentane	----	0.01	0.02	----	----
Hexane	----	0.01	0.05	0.01	----
Methylclcpentane	----	----	0.02	----	----
Benzene	24.	6.6	0.35	0.16	----
Toluene	0.12	0.18	0.55	0.03	0.01

*The quantity of each combustion product is reported in milligrams per gram of sample.

only in trace amounts after 300 C. Additionally, in the second fraction the maximum amount of vinyl chloride is formed. As expected, carbon dioxide and carbon monoxide reached their maxima at higher temperatures. Most straight-chain aliphatics reached their maxima in the third step and were present in the last step in very small quantities. Olefins began to form in the first step, reached their maxima in the third, and did not appear in the last two fractions. More detailed information concerning variation of combustion products with heating rate and air supply may be found in Reference 14.

Benzyl chloride analysis. Analysis for benzyl chloride was conducted independently of analysis for other combustion products and only on five commercial meat-wrap films. Heating procedure differed from the standard procedure. The 0.25-g samples were heated at the bottom of a 250-ml round-bottom flask enclosed in a heating mantle. In close proximity to the sample in the flask was a thermocouple which was used both to monitor and control the temperature. In some tests the sample and controlled thermocouple were placed at the bottom of a vial, and covered with about one cm of Mallcosorb^R to remove the hydrogen chloride gas. The vial was placed on the bottom of the heating flask.

The stopper in the flask contained two short glass tubes, one capped by a septum through which the evolved gases in the flask were sampled, using a 10-cc gas syringe. The other tube was connected to a small Saran^R plastic bag, which acted as an expansion chamber as the flask was heated. When the plastic reached the desired temperature (and periodically thereafter), one to three cc of gas were removed from the flask with a gas syringe, and transferred to either the gas chromatograph or the GC-MS30.

A six-foot-long, 1/4-in.-diameter column of 10 percent Carbowax 20 M on Chromosorb P was used to separate benzyl chloride from other products. At 100 C the net retention time of benzyl chloride was 36 minutes. This peak was positively identified as benzyl chloride by GC-MS.

Films A and B were heated to 200 C and 337 C (using the heating arrangement described) and held at these temperatures until past the emission of benzyl chloride. The heating cycle was begun at time zero and 30 to 60 minutes were required for the flask to attain the desired temperatures. The data, plotted in Figures 11 and 12, show 0.1 to 5 milligrams benzyl chloride per gram of sample. These runs were made without the use of Mallcosorb^R, except in one run as noted in Figure 11. Because the increase in benzyl chloride at the start of the runs corresponds with the increase in temperature, it is suspected that the amount of benzyl chloride is proportional to the temperature, with only a secondary dependence on heating rate, but this hypothesis should be veri-

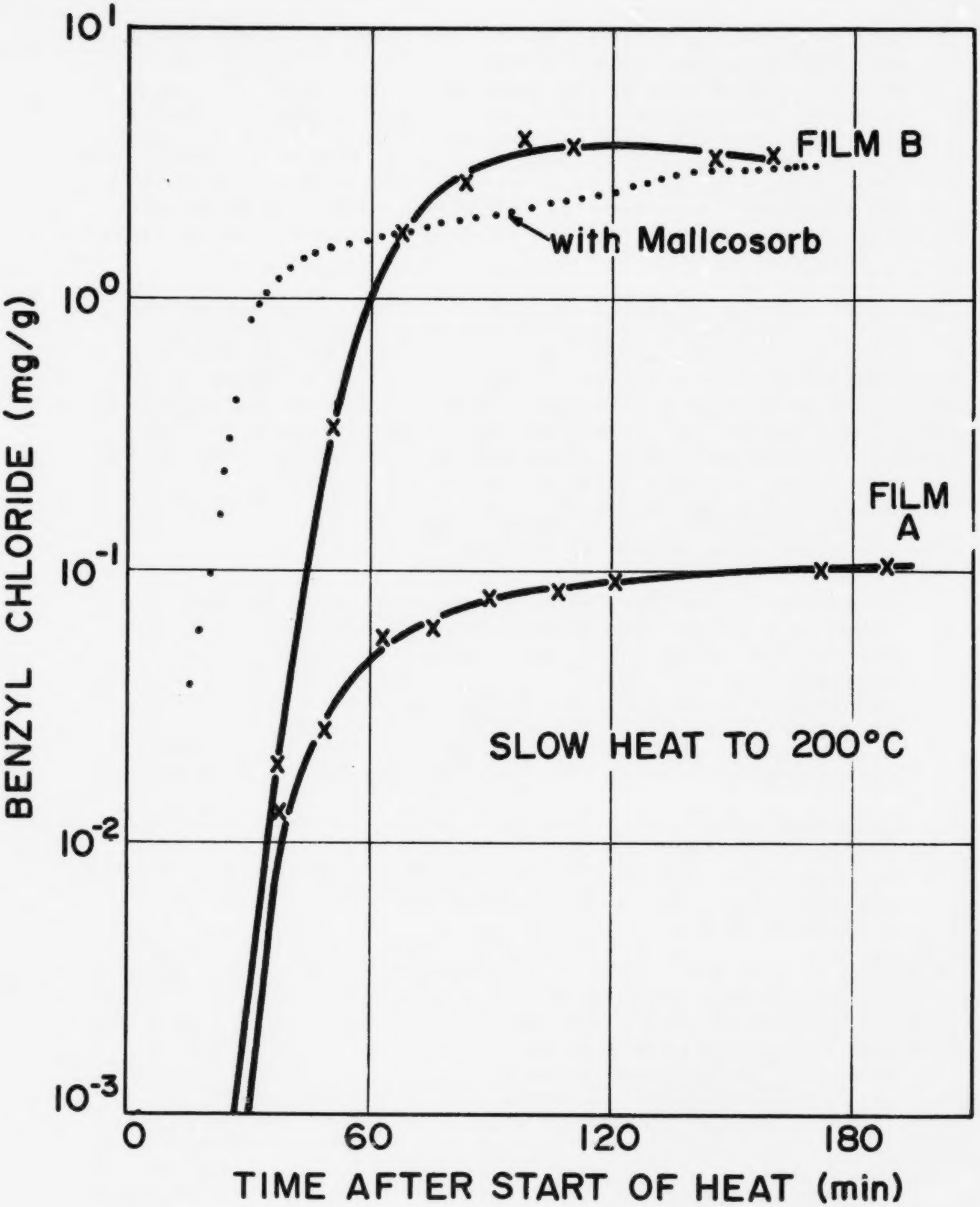


Figure 11. Benzyl chloride production by two meat-wrap films (A and B) heated slowly to 200 C

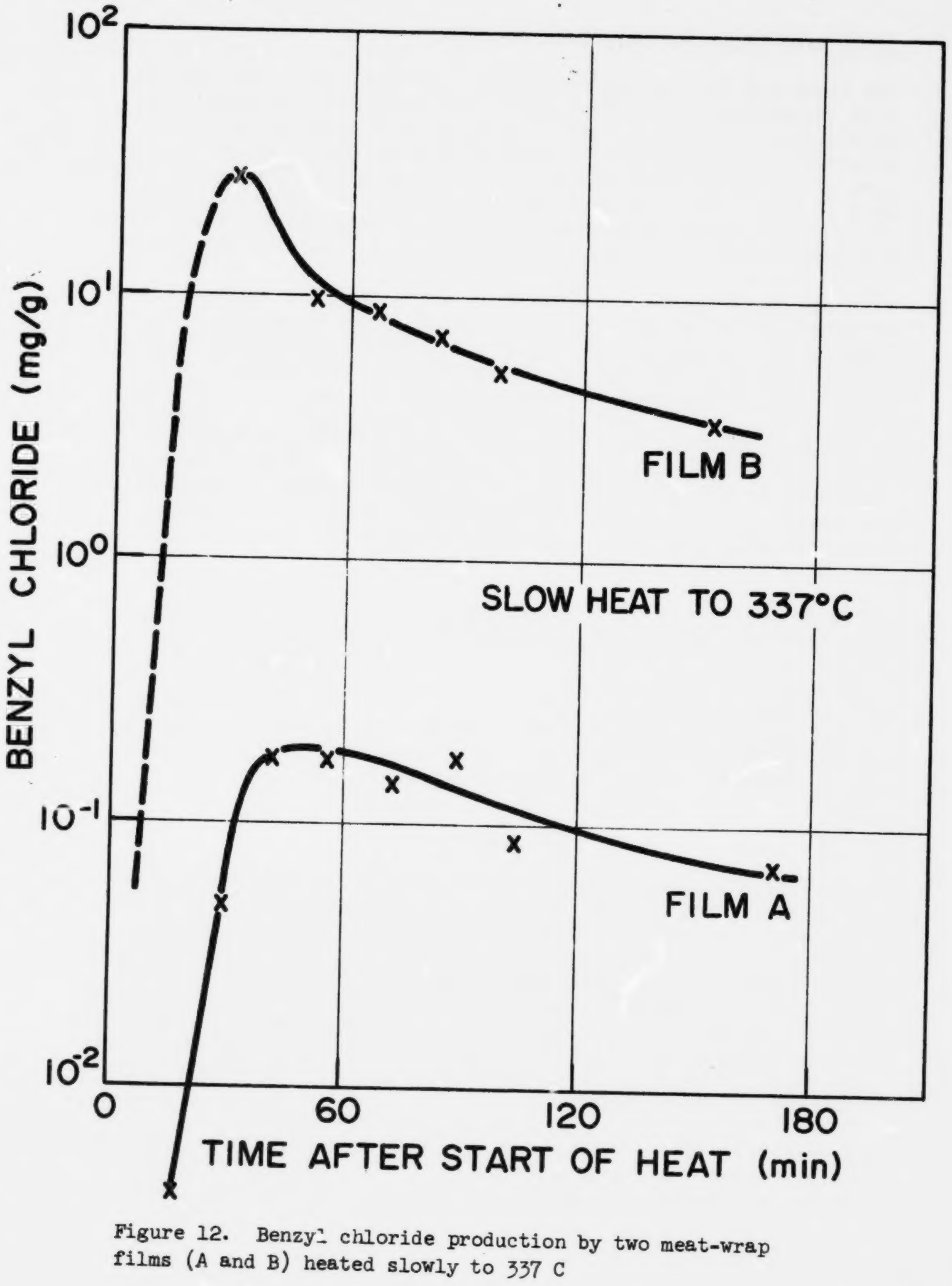


Figure 12. Benzyl chloride production by two meat-wrap films (A and B) heated slowly to 337 C

fied, especially for very fast heating.

The flask was then preheated to 200 C and the sample was dropped into the bottom of the flask which was immediately re-stoppered. Maintaining the flask at 200 C, samples were taken at periodic intervals, resulting in 0.01 to 5 milligrams benzyl chloride per gram of sample as shown graphically in Figure 13. Similarily, the data in Figure 14, showing 0.05 to 10 milligrams benzyl chloride per gram of sample, were obtained by preheating the flask to 337 C, and maintaining it at that temperature after inserting the sample.

Although these data confirm the conclusion that the maximum amount of benzyl chloride observed was primarily proportional to the temperature, (although testing only two temperatures), it must be pointed out that the faster heating rate is still considerably slower than encountered in hot-wire cutting.

Film C was identical to Film B and Film D was identical to Film A. Film E had an additive and produced slightly less benzyl chloride than Film A. The amount of benzyl chloride produced depends on the batch of plastic, with about one batch in 20 producing the larger amount. The reason for these batch differences has not been determined.

Phosgene analysis. Phosgene has occasionally been reported as a combustion product of PVC, although it has not been detected in any of our work. A report that this compound is produced only at high temperatures led us to propose a laser-pyrolysis study. A preliminary test with a carbon dioxide laser available to us at the University of Rochester was carried out but was unsuccessful because of insufficient power. It is hoped that the experiment can be repeated later with a higher-powered laser.

Discussion

Quantitative release of hydrogen chloride on thermal degradation of PVC presents a serious problem in its disposal. Incinerator stack gases may be wet-scrubbed, effectively removing hydrogen chloride. However, hydrogen chloride is still implicated in incinerator corrosion processes, even though these processes have not been fully elucidated.[8] The fact that the calcium carbonate-filled floor tile sample showed less hydrogen chloride than expected indicated there may be some promise in the method of spreading some such chemical on material to be incinerated in order to react with or absorb hydrogen chloride.

Our data fits rather well with a degradation mechanism proposed by Madorsky[5] involving rupture of the C-Cl bond followed by abstraction of an adjacent hydrogen atom, forming a double bond. The

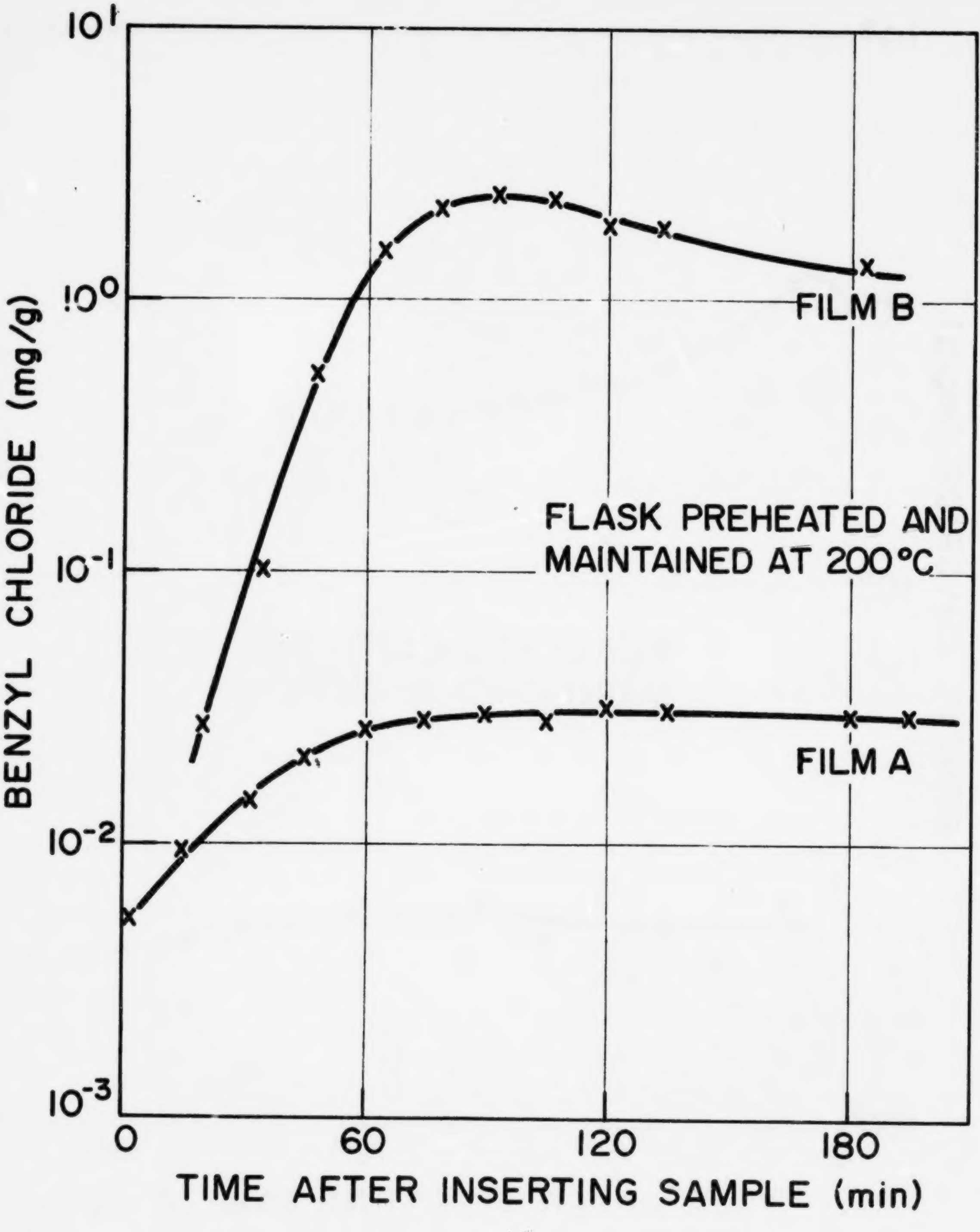


Figure 13. Benzyl chloride production by two meat-wrap films (A and B) heated at 200 C

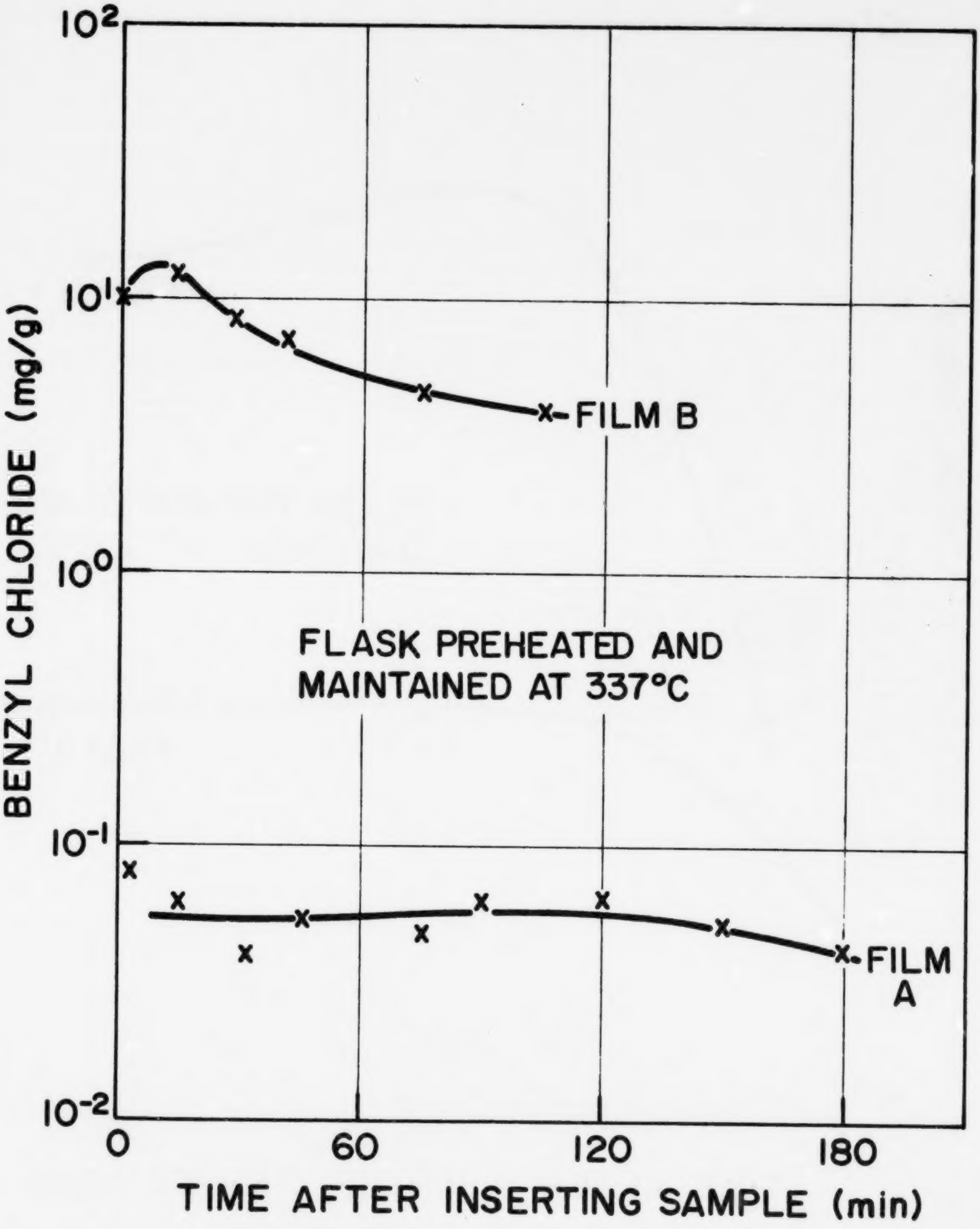


Figure 14. Benzyl chloride production by two meat-wrap films (A and B) heated at 337 C

chain reaction involves successive removal of chlorine atoms in the β position to the first double bond forming a chain with conjugated double bonds. Benzene is thermodynamically the most stable molecule that could be formed from the resulting chain containing conjugated double bonds. The fact that benzene forms during the same temperature range as hydrogen chloride and before other hydrocarbons is significant. Toluene and benzyl chloride could be formed by occasional skips in the randomly conjugated double-bond formation.

POLYSULFONE

Introduction

Polysulfone (Figure 15) is a specialty thermoplastic presently produced in comparatively small quantities for electrical, automotive, and appliance parts.[21] Primary interest in its combustion products was to account for its approximately 7.6 percent sulfur.

Samples

Two polysulfone samples in commercial pellet form were studied.

Results

Thermal analysis. Differential thermal analysis of polysulfone was carried out in both helium and air atmospheres using a 10-C/min heating rate (Figure 16). The plastic was liquid by 350 C, but no melting endotherms are evident. The only significant features of either curve are two exothermic peaks at 535 and 645 C in air, both corresponding to temperatures where production of volatile and nonvolatile products occurs very rapidly. Polysulfone thermogravimetric analysis records were also obtained in both helium and air atmospheres (Figure 17). The heating rate was 5 C/min. These records show a 62-percent weight loss between 460 and 520 C in helium, while in air a 55-percent weight loss occurs more rapidly between 460 and 500 C. The remaining 45 percent of the weight in air is lost much more gradually above 510 C. Davis has shown that crosslinking is an important factor in polysulfone degradation,[22] although chain scission is also involved.

Qualitative analysis. Absorption bands characteristic of carbon dioxide, carbon monoxide, carbonyl sulfide, and sulfur dioxide appear in the infrared spectrum of polysulfone combustion products (Figure 18). The spectrum was obtained using a 10-cm path-length gas cell. Hydrogen sulfide has been reported as a combustion product of polysulfone,[23] but it would not be observed in small quantities with either the infrared spectrophotometer or the hydrogen flame gas chromatograph detector used in this study. Methane, ethylene, and ethane were separated by gas chromatography on a six-foot-long, 1/4-in.-diameter Porapak Q column. Benzene, toluene, ethylbenzene, and styrene were separated on a 12-foot-long, 1/4-in.-diameter column of 5 percent Squalane on Chromosorb P. Those were the only gaseous products identified. Thirty to fifty percent of the polysulfone combusted formed liquid residue which condensed in the combustion tube or sample bag. Components of this liquid residue were separated on a 13-in.-long, 1/4-in.-diameter low K' Durapak column (Figure 19) and have been characterized or identi-

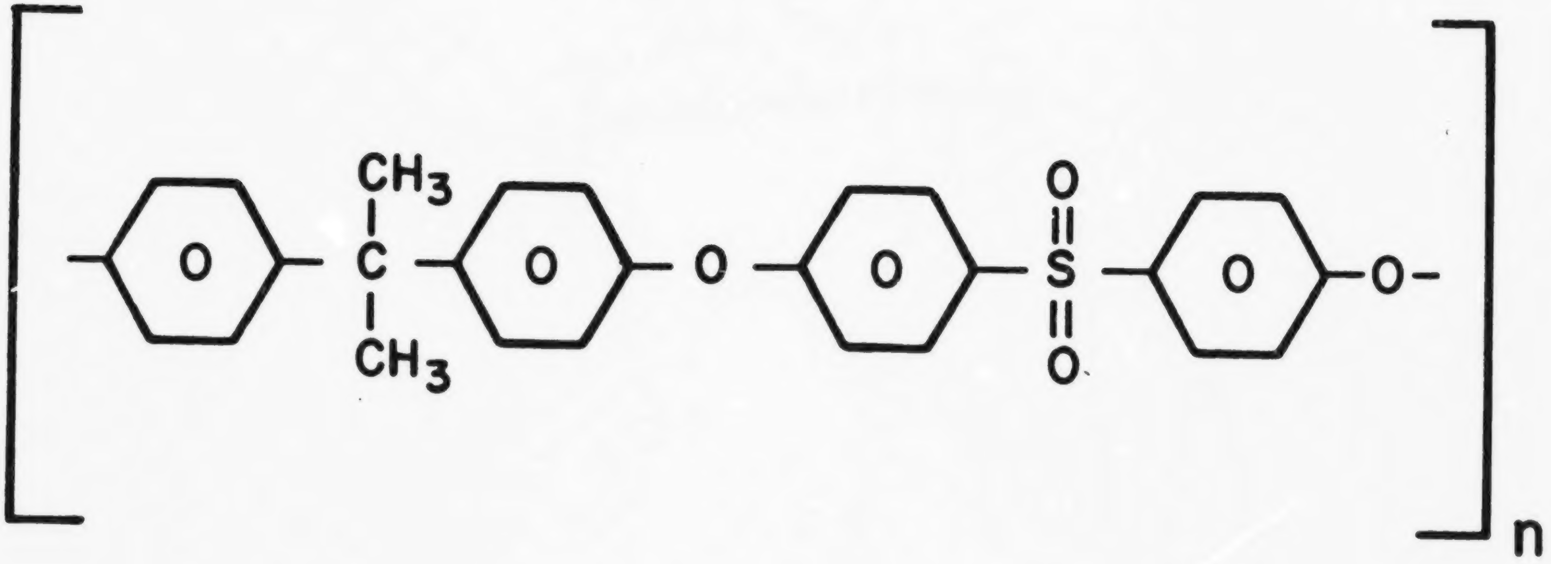


Figure 15. Bisphenol A-polysulfone

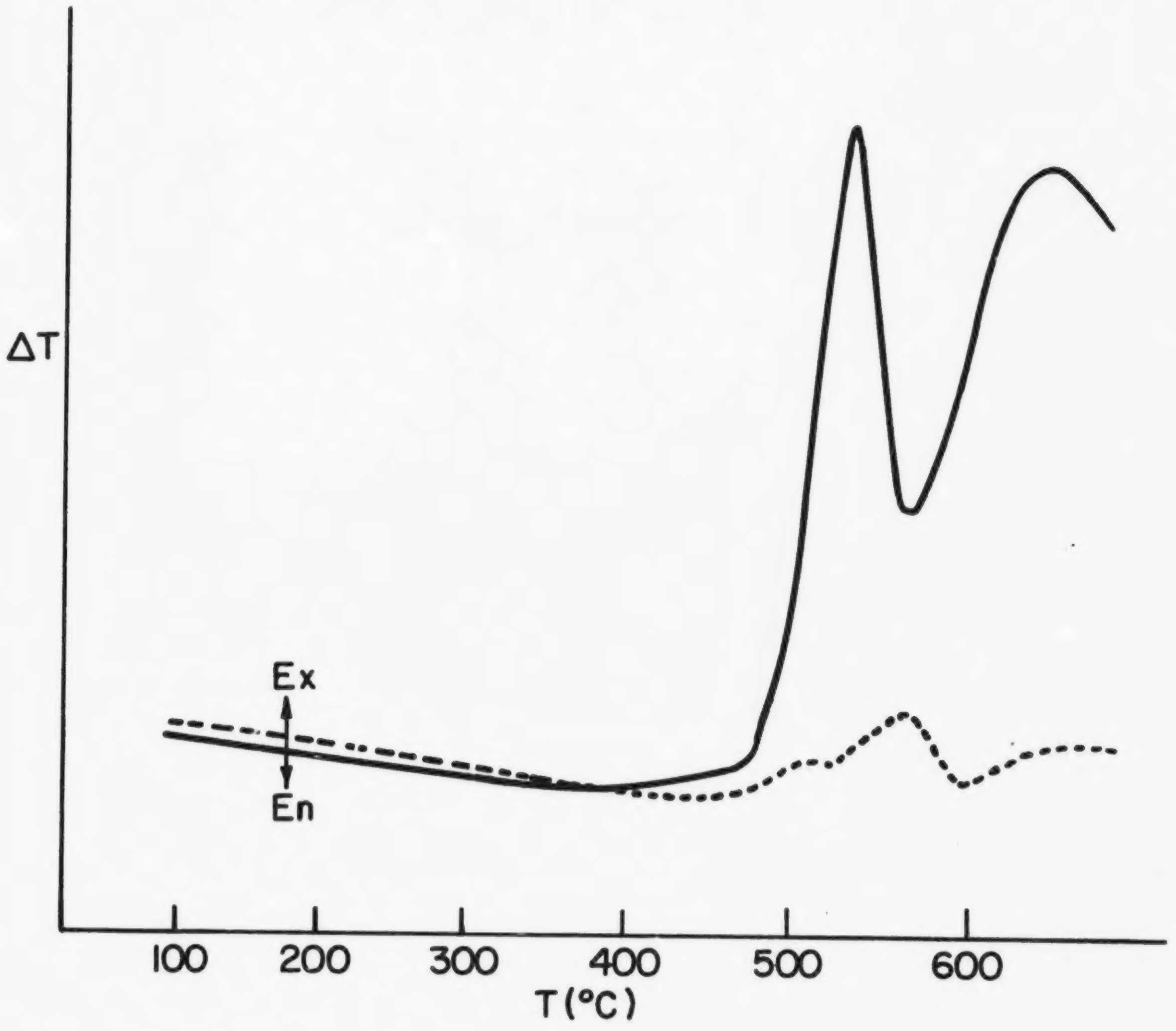


Figure 16. Differential thermal analysis records of polysulfone heated at 10 C/min in helium (broken curve) and air (smooth curve)

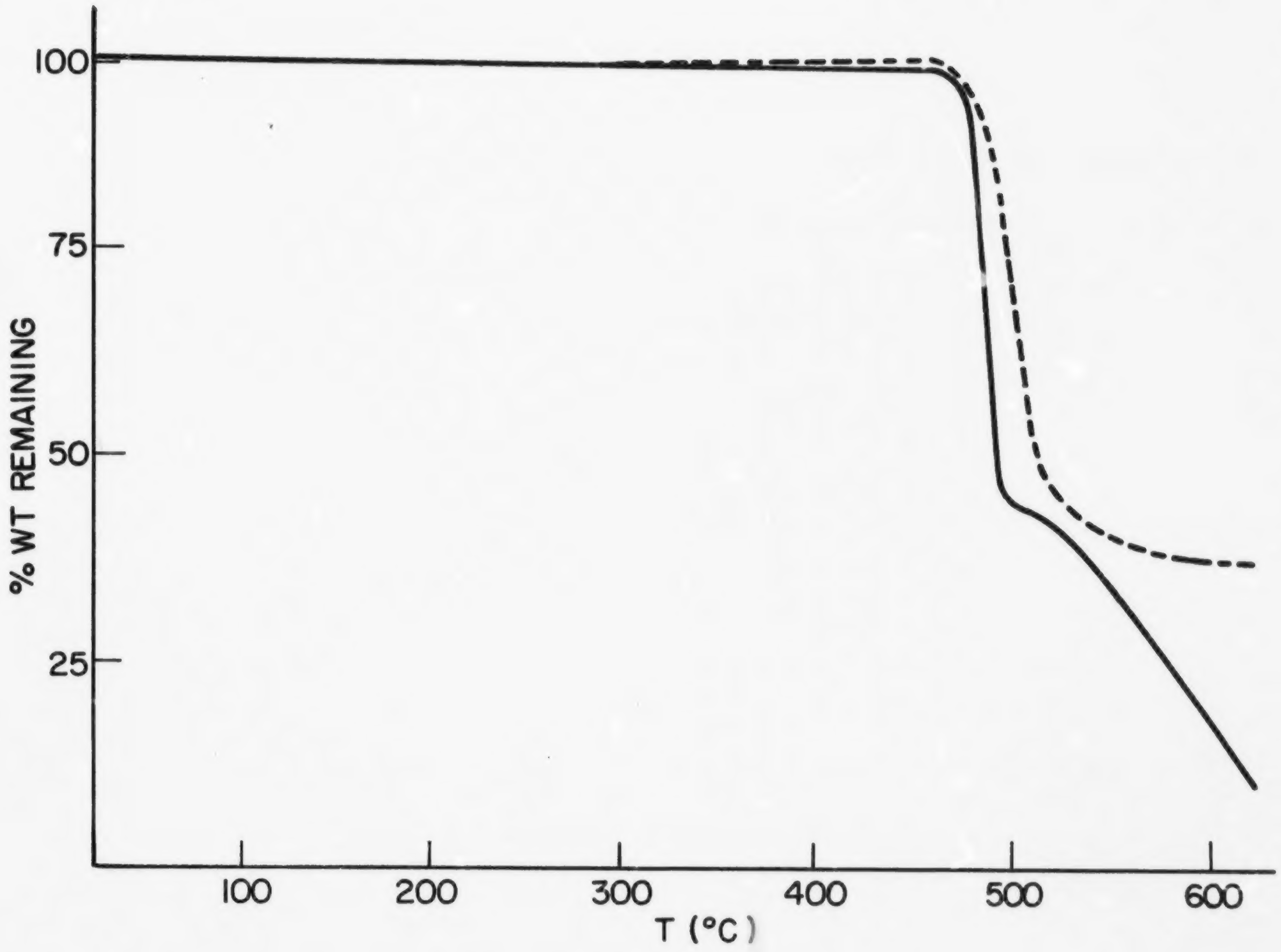


Figure 17. Thermogravimetric analysis records of polysulfone heated at 5 C/min in helium (broken curve) and air (smooth curve)

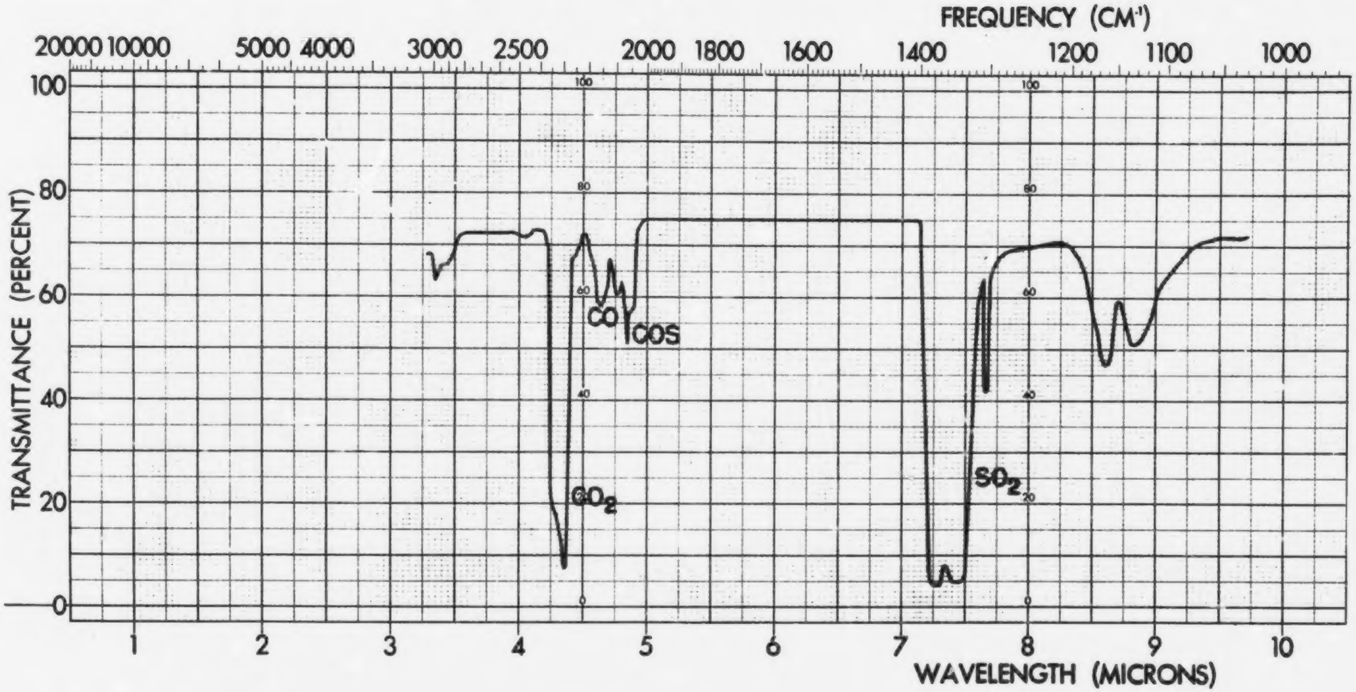


Figure 18. A portion of an infrared spectrum of polysulfone combustion products (10-cm path-length gas cell)

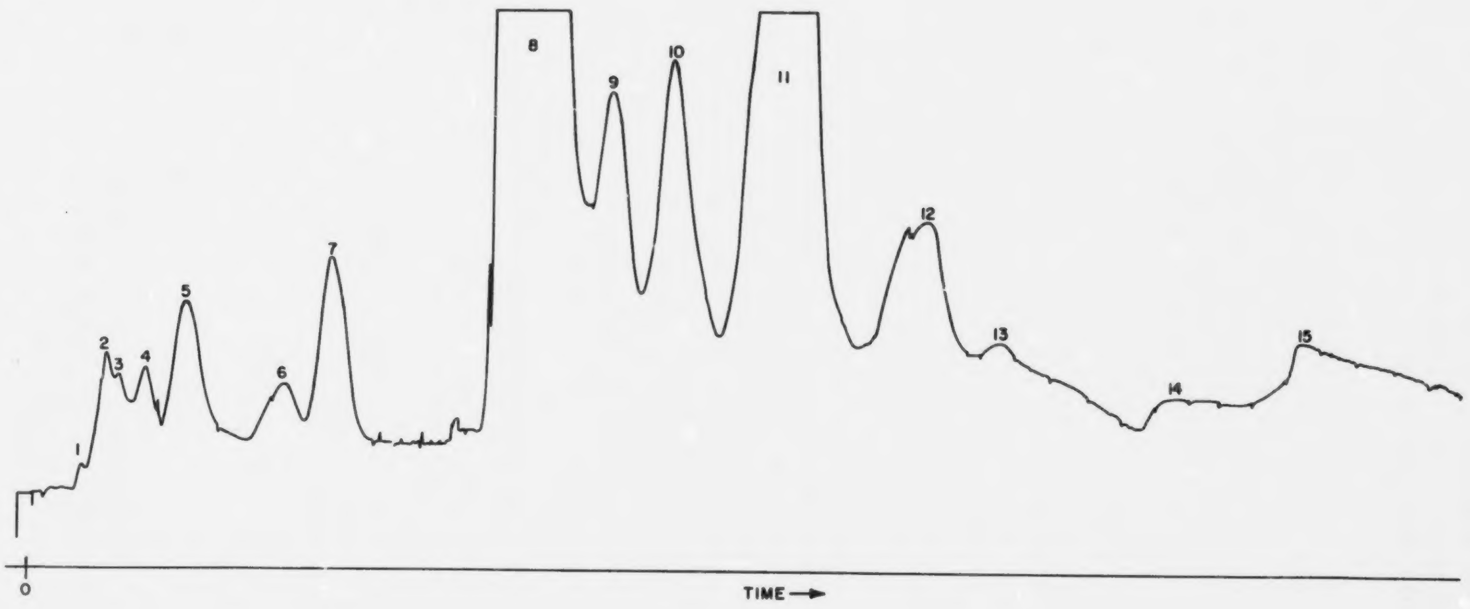


Figure 19. Chromatogram of polysulfone liquid residue on a low K' Durapak column

fied (Table 5). Major components of the liquid residue are phenol, cresol, and phenyl-p-tolyl ether. Isomers were difficult to distinguish as many peaks were due to multicomponent mixtures of products.

Quantitative analysis. Polysulfone samples for quantitative analysis were heated rapidly from room temperature to 350 C and then programmed at 5 to 50 C/min to either 800 or 1000 C. Table 6 shows quantities of eight gaseous products produced by one of the polysulfone samples at five combustion conditions with the 800 C temperature maximum. Carbon dioxide, carbon monoxide, and sulfur dioxide were quantitated by infrared spectroscopy using a 10-cm path-length gas cell. Sulfur dioxide, however, tended to dissolve in any moisture present in the cell and to be adsorbed onto metal parts, thus leading to erratic results. It was quantitated again by ultraviolet spectrophotometry[12] at each of the combustion conditions. The two polysulfone samples tested had 7.62 and 7.56 percent sulfur, and so about 76 mg sulfur had to be accounted for in each gram of plastic. The hydrocarbons were quantitated by gas chromotography on the same columns used for their separation. Quantities in Table 6 show no discernable trends.

Quantities of combustion products of polysulfone using the 1000 C temperature maximum are shown in Table 7. Results for the two samples were averaged and were often nearly identical, as indicated by the calculated deviations which include differences between the two samples as well as experimental error and the randomness of the combustion process. In all cases over 85 percent of the sulfur of polysulfone is accounted for as sulfur dioxide. Volatile products identified account for 50 to 60 percent of the plastic combusted, the remaining 40 to 50 percent being liquid residue. Quantities of compounds produced during several temperature ranges chosen on the basis of the TGA curve are shown in Table 8. Carbon dioxide and carbon monoxide are absent below 450 C and only a small amount of the latter is formed by 490 C. Sulfur dioxide is formed primarily between 490 and 550 C, where carbonyl sulfide is also found. This compound was probably too dilute to be detected in samples taken over the entire temperature range of 0 to 1000 C. Aliphatic hydrocarbons peak in the third temperature range while aromatic hydrocarbons peak in the fourth. Again, over 90 percent of the sulfur and about 60 percent of the plastic is accounted for.

Discussion

Thermal degradation of polysulfone seems to proceed by chain scission so that most of the sulfur is released as sulfur dioxide. Relatively small amounts of carbonyl sulfide and possibly hydrogen sulfide also formed. The most significant hydrocarbon products, toxicologically, were found in the liquid residue.

TABLE 5

IDENTIFICATION OF POLYSULFONE RESIDUE CHROMATOGRAM PEAKS

Peak Number	Molecular Weight	Identification
1	92	Toluene
2	106	Ethylbenzene (or Xylene)
3	104	Styrene
4	120	Methyl ethylbenzene*
	126	Chlorotoluene?
5	106	Benzaldehyde
	118	Benzofuran
	116	Indene
6	132	Methylbenzofuran
	130	Methylindene
	120	Trimethylbenzene*
7	128	Naphthalene
	142	Methylnaphthalene
8	94	Phenol†
	154	Biphenyl
9	170	Diphenyl ether (or Phenyl phenol)
10	108	Cresol
11	168	Dibenzofuran
	184	Phenyl-p-tolyl ether†
	156	Dimethylnaphthalene
	122	Ethylphenol
12	198	aryl-Ethylphenyl phenyl ether*
13	212	2-Hydroxyphenyl-2-phenyl propane
14	226	Unidentified
15	224	Unidentified

* Or isomer

† Major component

TABLE 6

COMBUSTION PRODUCTS OF POLYSULFONE AT SEVERAL COMBUSTION CONDITIONS
(800 C miximum)

Air flow, cc/min	65	98	98	200	450
Oxygen flow, cc/min	--	--	20	--	--
Heating Rate, C/min	5	5	5	5	50
Carbon dioxide*	1331	1044	1148	1661	1488
Carbon monoxide	298	363	253	437	265
Sulfur dioxide-IR	204	152	132	189	179
Sulfur dioxide-UV	150	149	149	152	150
Methane	19.0	18.0	32.6	14.8	16.2
Ethylene	0.77	0.53	0.73	0.41	0.67
Ethane	0.68	0.86	0.72	0.67	0.74
Benzene	5.23	5.71	4.34	4.45	6.47
Toluene	2.19	2.52	1.55	1.96	3.71
%Sulfur accounted for (UV)	98.7	98.0	98.0	100.	98.7
%Plastic accounted for	67.	62.	61.	82.	70.
%Residue (by difference)	33.	38.	39.	18.	30.

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 7

COMBUSTION PRODUCTS OF POLYSULFONE AT SEVERAL COMBUSTION CONDITIONS (1000 C maximum)

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	1072 ± 125	861 ± 47	1414 ± 82
Carbon monoxide	250 ± 4	261 ± 9	87 ± 6
Sulfur dioxide	145 ± 1	139 ± 8	131 ± 4
Methane	28.4 ± 0.4	9.68 ± 0.20	23.5 ± 0.10
Ethylene	0.76 ± 0.02	0.63 ± 0.16	1.17 ± 0.06
Ethane	0.72 ± 0.03	0.60 ± 0.18	0.60 ± 0.03
Benzene	5.39 ± 0.03	4.76 ± 0.01	8.69 ± 1.57
Toluene	2.59 ± 0.01	2.16 ± 0.25	3.61 ± 1.17
Ethylbenzene	0.60 ± 0.03	0.53 ± 0.06	0.67 ± 0.13
Styrene	0.12 ± 0.01	0.12 ± 0.04	0.20 ± 0.08
%Sulfur accounted for	95.6	91.6	86.0
%Plastic accounted for	58	50	59
%Residue (by difference)	42	50	41

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 8

POLYSULFONE COMBUSTION PRODUCTS DURING SEVERAL TEMPERATURE RANGES

Compound	<450 C	450 - 490 C	490 - 550 C	>550 C	Total
Carbon dioxide*	----	----	31	1104	1135
Carbon monoxide	----	2.28	35	213	250
Sulfur dioxide	6.75	29.3	93	11.3	140
Carbonyl sulfide	----	----	0.52	----	0.52
Methane	0.38	2.86	10.2	6.59	20.0
Ethylene	0.01	0.10	0.39	0.33	0.83
Ethane	0.01	0.06	0.33	0.14	0.54
Benzene	----	0.10	1.64	3.82	5.56
Toluene	0.01	0.02	0.54	1.18	1.75
Ethylbenzene	0.01	----	0.04	0.37	0.42
Styrene	----	----	----	----	----
%Sulfur accounted for					92.6
%Plastic accounted for					60
%Residue (by difference)					40

*The quantity of each combustion product is reported in milligrams per gram of sample.

POLYURETHANE

Introduction

Polyurethane applications include furniture, mattresses and pillows, and automobile interiors. Interest in combustion products of polyurethanes stems from three considerations: first, although not produced in as large quantities as polyethylene or polyvinyl chloride, polyurethanes can contribute significantly to the overall incineration problem because of their use for articles which are so bulky they are difficult to burn efficiently. Second, such articles tend to smolder in an accidental fire producing fumes of unknown toxicity. Third, the isocyanate materials used in polyurethane production can cause severe sensitization reactions in some people. Because of isocyanate contact during polyurethane production,[24] most studies of the toxicity of polyurethane or its combustion products have been directed toward analysis of any isocyanate present. The current study has been directed toward the lower-boiling combustion products and has not yet been extended to include isocyanates.

Samples

Six commercial polyurethane samples were analyzed. Four were foam samples of the type used for automobile seats and carpet backing, and are listed as follows:

Foam A	4.74 % N
Foam B	4.62 % N
Foam C	5.57 % N
Foam D	4.26 % N

In addition, two samples in pellet form were obtained: Sample E, an aromatic methylene diisocyanate compound containing 4.15 percent nitrogen; and Sample F, an H_{12}-aliphatic methylene diisocyanate compound containing 4.07 percent nitrogen. Both are of the polyester type.

Results

Thermal analysis. The differential thermal analysis record of one of the foam samples (Figure 20) shows an exothermic doublet between 290 and 375 C, peaking at 310 C. No endotherms are evident. The thermogravimetric analysis record of a foam sample (Figure 21) shows a two-step degradation, the first and largest step beginning at about 260 C and ending at about 310 C, during which 77 percent of the weight is lost. The remaining step is very gradual and the plastic is completely combusted by 575 C. Thermogravimetric analysis of the aromatic pellet sample (Figure 22) shows that the same two-step degradation occurs but at higher temperatures.

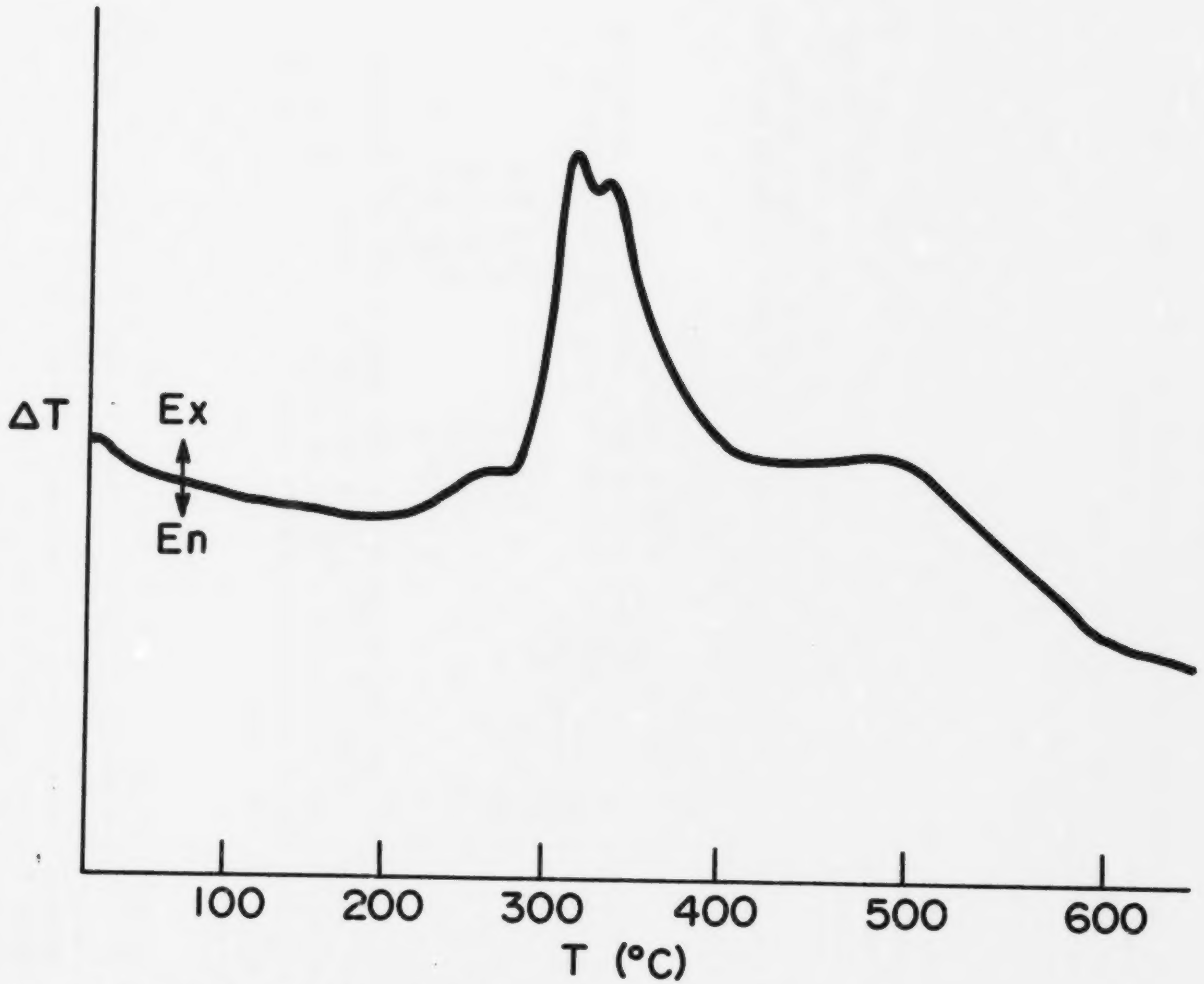


Figure 20. Differential thermal analysis record of a polyurethane foam heated at 10 C/min in air

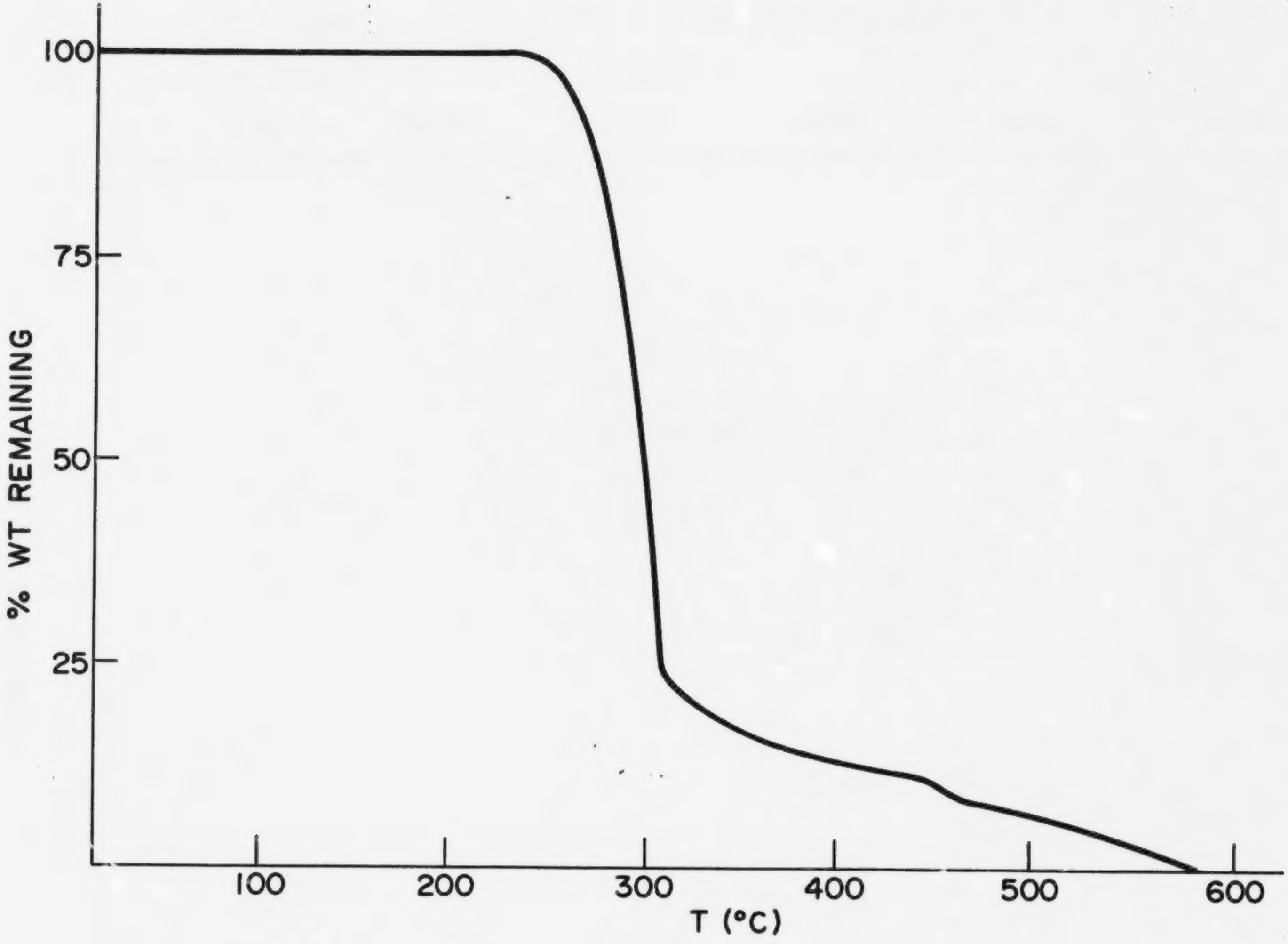


Figure 21. Thermogravimetric analysis record of a polyurethane foam heated at 10 C/min in air

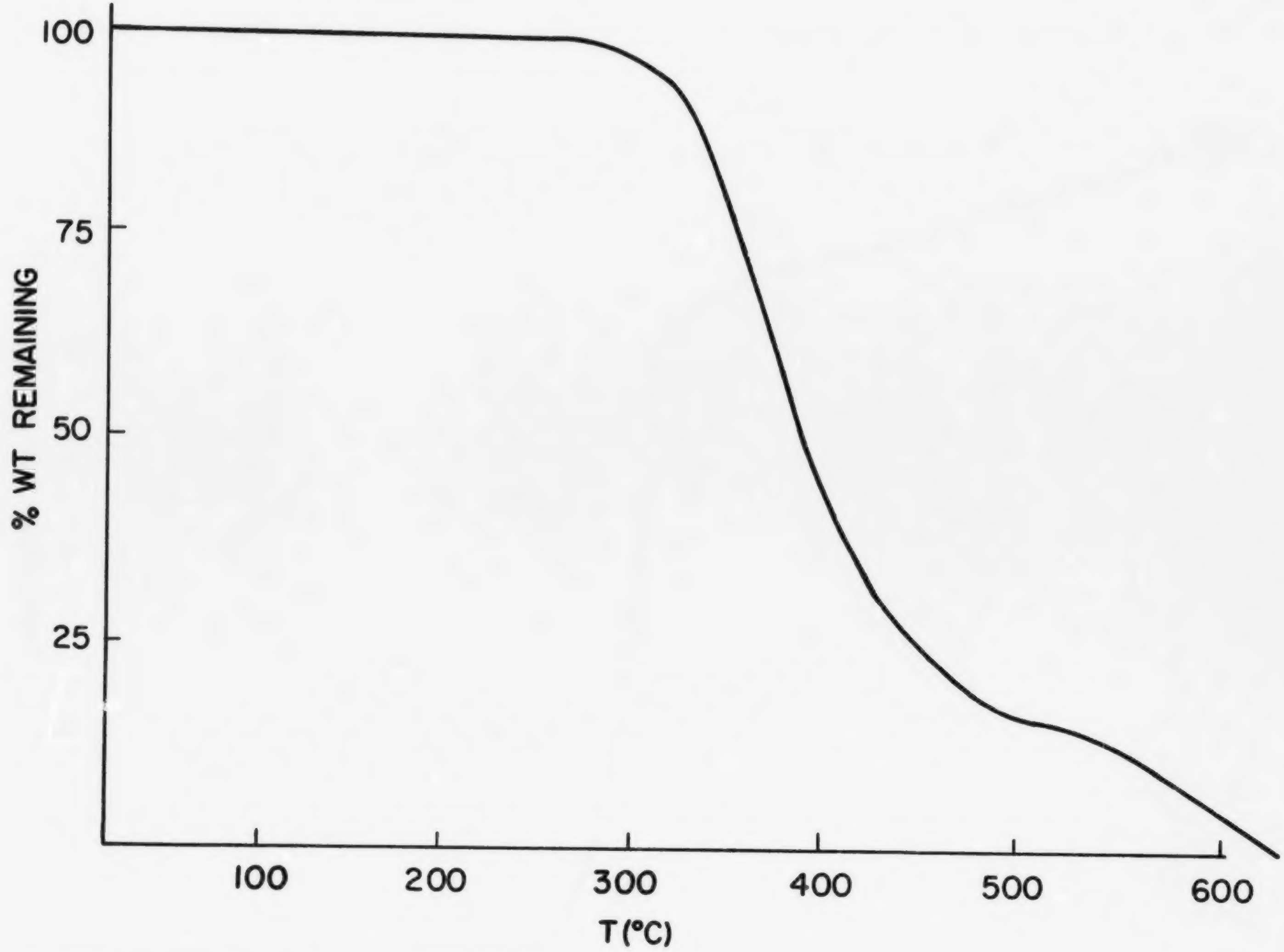


Figure 22. Thermogravimetric analysis record of polyurethane Sample E heated at 10 C/min in air

Sample E does not begin to lose weight until 300 C and then loses 85 percent of its weight by 500 C. The remainder of the weight is lost more gradually up to 625 C.

Qualitative analysis. Qualitative analysis of combustion gas from the polyurethane foam samples by infrared spectroscopy using a 10-cm path-length gas cell revealed bands due to carbon dioxide, carbon monoxide, methanol, and acetaldehyde. The pellet samples did not produce the latter two compounds. For the foam samples, C_1-through C_3-hydrocarbons, hydrogen cyanide, and cyanogen were separated using a six-foot-long, 1/4-in.-diameter Porapak Q column while methanol, acetaldehyde, propionaldehyde, and acetone were separated on a six-foot-long, 1/4-in-diameter column of 10 percent Carbowax 20 M on Chromosorb P. Compounds were identified by mass spectrometry. The pellet samples were analyzed later in the study and a six-foot-long, 1/4-in.-diameter column of Durapak n-Octane/Porasil C was used for separation of products because its resolution of hydrocarbon isomers was superior to that of Porapak Q. C_1-through C_6-hydrocarbons could be analyzed using the Durapak column, but not oxygen-containing compounds such as methanol and acetone. Preliminary GC-MS analysis of liquid residues formed on combustion of polyurethanes has shown that toluidine and either aniline or methylpyridine are significant components. Halogenated compounds were observed but not positively identified. The present study of polyurethane combustion products is incomplete and many volatile and nonvolatile products remain to be identified. Other studies [25,26] have identified more nitrogen-containing products such as acetonitrile, acrylonitrile, pyridine, and phenylisocyanate. Products have not been quantitated, however, and parts of these studies were done under pyrolysis conditions.

Quantitative analysis. Products, except hydrogen cyanide and carbon oxides, were quantitated on the chromatograph columns used for their separation. Carbon dioxide and carbon monoxide were quantitated by infrared spectroscopy. Cyanide ion was quantitated using an Orion specific ion electrode and an Orion 801 digital pH meter. This electrode measures only cyanide ion and not the equally toxic organic cyanide compounds (nitriles). Ammonia was quantitated using an Orion ammonia-specific electrode. Oxides of nitrogen from several foam samples were quantitated by the Saltzman method but were found to be in the microgram per gram range. Tables 9 and 10 show milligrams of identified combustion products per gram of foam sample when four foams were combusted under several different conditions. Cyanide ion, calculated as hydrogen cyanide, ranges from 7 to 46 milligrams per gram of sample and accounts for 9 to 53 percent of the nitrogen of the plastic combusted. A significant decrease in cyanide ion is noted at the faster heating rate, indicating it is either broken down or not formed as efficiently at higher temperatures. Other products, and the hydrocarbons in particular, increase considerably at the

TABLE 9

COMBUSTION PRODUCTS OF POLYURETHANE FOAMS A AND B AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
	Foam A		
Carbon dioxide*	712.	661.	533.
Carbon monoxide	193.	207.	169.
Cyanide ion (as HCN)	46.2	34.6	19.3
Ammonia	1.60	4.42	0.24
Methane	1.73	2.02	21.2
Ethylene	1.95	3.55	16.9
Ethane	0.18	0.60	3.9
Propylene	2.31	10.55	67.3
Propane	0.22	0.60	7.3
Methanol	13.2	9.3	6.6
Acetaldehyde	17.7	20.5	10.2
Propionaldehyde	7.2	13.7	7.8
Acetone	13.6	14.0	12.5
%Nitrogen accounted for	53.3	45.4	21.1
%Plastic accounted for	38.3	38.2	42.8
	Foam B		
Carbon dioxide	657.	568.	521.
Carbon monoxide	116.	159.	211.
Cyanide ion (as HCN)	40.5	32.7	19.3
Ammonia	N.A.†	N.A.	N.A.
Methane	1.86	2.23	21.6
Ethylene	2.32	4.01	17.6
Ethane	0.33	0.73	5.0
Propylene	2.84	10.40	42.8
Propane	0.30	0.40	10.7
Methanol	13.6	4.7	14.2
Acetaldehyde	18.2	20.9	28.5
Propionaldehyde	7.5	17.7	21.9
Acetone	15.2	15.6	34.3
% Nitrogen accounted for	45.5	36.7	21.6
%Plastic accounted for	33.1	33.2	44.8

*The quantity of each combustion product is reported in milligrams per gram of sample.

†Not analyzed.

TABLE 10

COMBUSTION PRODUCTS OF POLYURETHANE FOAMS C AND D AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
	Foam C		
Carbon dioxide*	591.	836.	480.
Carbon monoxide	165.	235.	241.
Cyanide ion (as HCN)	34.7	32.5	11.6
Ammonia	0.23	0.09	0.01
Methane	2.40	2.41	27.3
Ethylene	1.57	3.08	15.5
Ethane	0.27	0.32	3.5
Propylene	3.56	10.60	61.1
Propane	0.37	0.68	8.3
Methanol	26.4	19.7	26.0
Acetaldehyde	27.1	32.5	53.9
Propionaldehyde	2.4	3.1	16.2
Acetone	12.4	11.1	39.8
%Nitrogen accounted for	32.3	30.3	10.8
%Plastic accounted for	34.3	44.5	49.8
	Foam D		
Carbon dioxide	570.	486.	395.
Carbon monoxide	295.	275.	311.
Cyanide ion (as HCN)	23.1	27.0	7.3
Ammonia	N.A.†	N.A.	N.A.
Methane	2.65	1.42	36.0
Ethylene	3.26	2.11	24.7
Ethane	0.38	0.25	6.5
Propylene	5.80	4.76	79.7
Propane	0.84	0.54	17.2
Methanol	33.5	20.7	31.2
Acetaldehyde	26.8	35.4	70.2
Propionaldehyde	3.2	4.5	18.8
Acetone	15.5	15.0	45.6
%Nitrogen accounted for	28.1	32.9	8.9
%Plastic accounted for	39.6	36.3	57.8

*The quantity of each combustion product is reported in milligrams per gram of sample.

†Not analyzed.

TABLE 11

COMBUSTION PRODUCTS OF POLYURETHANE SAMPLE E AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	361.	482.	267.
Carbon monoxide	110.	191.	49.
Cyanide ion (as HCN)	34.1	26.9	7.28
Ammonia	0.09	0.01	0.05
Methane	4.78	3.17	3.83
Ethylene	1.15	1.13	5.74
Ethane	1.82	1.61	1.28
Propylene	3.16	2.89	4.63
Propane	1.19	1.36	0.90
1-Butene	1.39	1.42	2.42
Butane	1.00	1.02	0.74
trans-2-Butene	7.80	8.08	14.2
cis-2-Butene	0.29	0.28	0.45
Pentane	1.10	1.19	0.37
1,3-Pentadiene?	11.4	12.2	7.71
1-Hexene	0.04	0.04	0.04
2-Hexene	0.17	0.22	0.19
%Plastic accounted for	21.5	27.5	14.3

*The quantity of each combustion product is reported in milligrams per gram of sample.

faster heating rate, perhaps because the polymer breaks down at such a low temperature that carbon dioxide and carbon monoxide are not efficiently formed. In most cases the volatile products quantitated account for 30 to 50 percent of the foam combusted. Quantities of combustion products of Samples E and F at three combustion conditions are listed in Tables 11 and 12. Cyanide ion again decreases at the faster heating rate. Samples D and F appear to generate more cyanide ion at the 40-cc/minute oxygen flow indicating that the trend of polyurethane cyanide ion generation cannot be safely generalized. Amounts of hydrocarbons generated are in the 1-to 10-milligram per gram range, and increase somewhat at the faster heating rate. The pentadiene identification has not been confirmed. Only 15 to 30 percent of these samples can be accounted for by the volatile products thus far identified. Although a considerable amount of liquid residue formed on combus-

TABLE 12

COMBUSTION PRODUCTS OF POLYURETHANE SAMPLE F AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	380.	690.	259.
Carbon monoxide	164.	223.	98.
Cyanide ion (as HCN)	15.1	40.5	6.47
Ammonia	0.09	2.03	0.09
Methane	2.89	1.50	3.37
Ethylene	6.68	4.20	4.12
Ethane	1.46	0.66	0.44
Propylene	10.6	3.65	10.0
Propane	0.89	0.78	0.45
1-Butene	1.78	1.73	2.86
Butane	0.45	0.66	0.19
trans-2-Butene	4.09	2.70	11.2
cis-2-Butene	0.27	0.12	0.24
1-Pentene	0.45	0.18	0.69
Pentane	0.31	0.12	N.A.†
1,3-Pentadiene?	5.56	2.52	5.74
1-Hexene	0.17	0.12	0.17
2-Hexene	0.45	0.38	0.42
%Plastic accounted for	31.3	34.6	15.8

*The quantity of each combustion product is reported in milligrams per gram of sample.

†Not analyzed.

tion of these samples, the amount of residue cannot be determined by difference because it is suspected that many more volatile products remain to be identified and quantitated.

Discussion

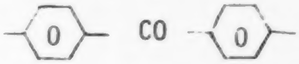
Studies to date indicate that combustion of polyurethanes may result in a wide variety of hydrocarbon and nitrogen-containing products. Carbon monoxide and cyanide are the only acutely toxic compounds identified. Neither would be expected to form in significant quantities during incineration, but large quantities could form during open burning or an accidental fire. Since carbon monoxide disrupts the bloods ability to carry oxygen and cyanide disrupts the cell's ability to use oxygen, there is a toxicological synergism between these two compounds making their combination particularly hazardous.

POLYIMIDE

Introduction

Polyimide is one of the most temperature-resistant plastics in use. It is currently produced in comparatively small quantities but is widely used in aircraft interiors and as wire insulation. Polyimide combustion products are of concern primarily from the standpoint of safety in an accidental combustion. Its formula (Figure 23) includes an aromatic group R which can be varied to obtain plastics of somewhat different properties. Synthesis and possible R groups of this polymer are described in the literature.[27]

Sample

One polyimide film sample was studied. It was found by analysis to be composed of 7.09 percent nitrogen, indicating that 71 milligrams of nitrogen per gram of sample should be accounted for in its combustion products. The R group was not known for certain, but  fits well with the nitrogen analysis.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis of polyimide in air (Figure 24) showed a one-step degradation which did not begin until about 500 C. The plastic was completely combusted by 650 C. This is consistant with findings of Heacock & Berr,[28] who report, in addition, a one-step degradation in helium beginning at the same temperature but with only a 30-percent weight loss up to 1000 C.

Qualitative analysis. Infrared analysis of polyimide combustion gas using a 10-cm path-length cell showed the presence of carbon dioxide, carbon monoxide, ammonia, and cyanide (Figure 25). On one occasion the scale-expanded infrared spectrum of polyimide gaseous products showed evidence of nitrous oxide but no ammonia. Gas chromatographic analysis of polyimide combustion gas showed the fewest compounds of any plastic tested. On a six-foot-long, 1/4-in.-diameter Porapak Q column five peaks appeared: two due to air, one due to carbon dioxide, one due to a combination of water and cyanogen, and another due to hydrogen cyanide. All identifications were made by mass spectrometry using an AEI MS-10. Nitric oxide, nitrogen dioxide, nitrous oxide, and ammonia were suspected but could not be detected using a hydrogen flame gas chromatograph detector. On a six-foot-long, 1/4-in.-diameter column of 10 percent Carbowax 20 M on Chromosorb P several other gaseous products appeared, benzene and benzonitrile being the only compounds identified by mass spectrometry. Polyimide produces a very small amount of condensed liquid residue on combustion. This residue was ana-

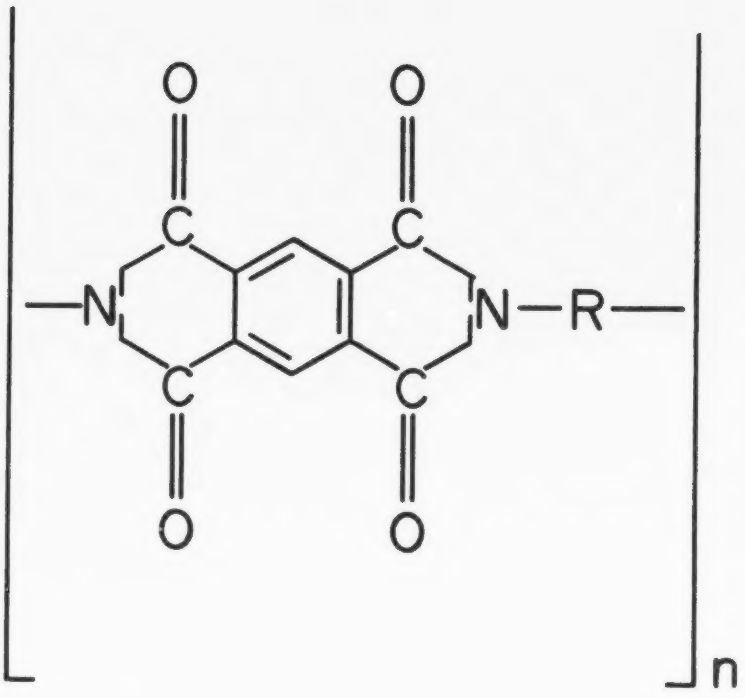


Figure 23. Polyimide

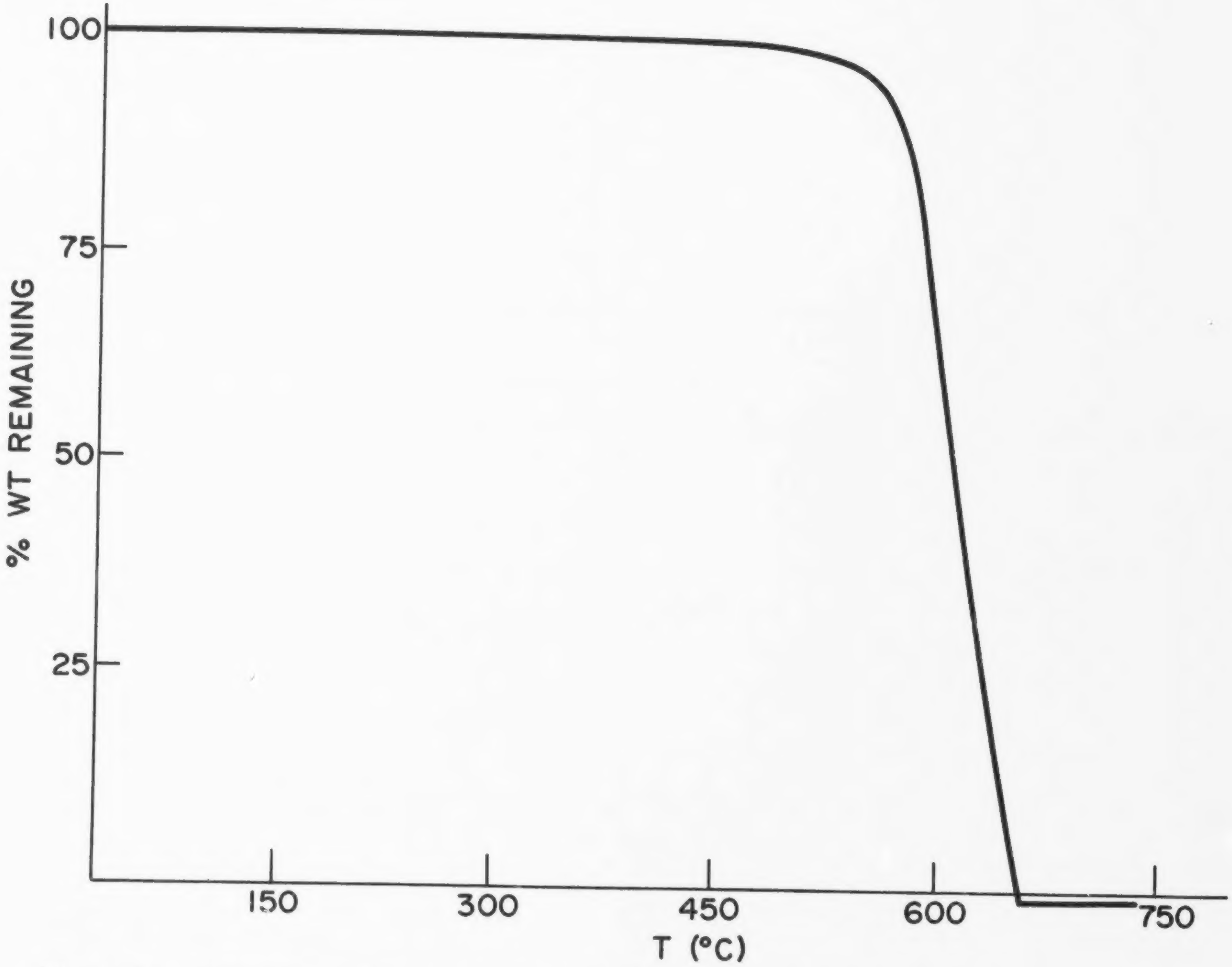


Figure 24. Thermogravimetric analysis record of polyimide heated at 10 C/min in air

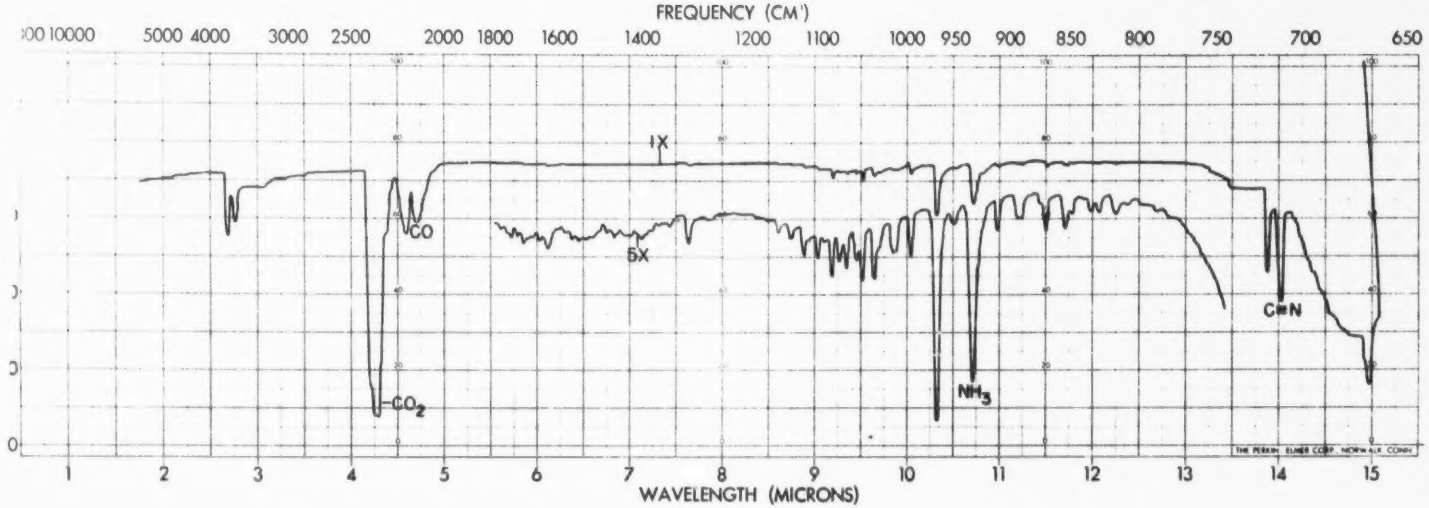


Figure 25. Infrared spectrum of polyimide combustion gas (10-cm path-length gas cell)

lyzed using the GC-MS 30 combination and was found to be rich in nitrogen-containing products (Table 13).

TABLE 13

IDENTIFICATION OF POLYIMIDE RESIDUE COMBUSTION PRODUCTS

GC Peak Number	Molecular Weight	Identification
1	---	Possibly water
2	87	N,N-Dimethyl acetamide
3	73	N-Methyl acetamide
	101	Diacetamide
4	59	Acetamide
	93	Aniline
5	67 or 69	Unidentified
6	94	Phenol
7	---	Unidentified
8	129	Diacetylethylamine?
9	---	Unidentified
10	---	Unidentified

Quantitative analysis. Carbon dioxide and carbon monoxide, quantitated by infrared spectrophotometry, accounted for a very large percentage (75 to 81) of the polyimide combusted, probably because of the high temperature at which degradation begins to occur (Table 14). Water vapor, not quantitated, would account for a significant portion of the remaining plastic. The quantities in Table 14 were obtained using the 0-to 800-C temperature range.

TABLE 14

CARBON DIOXIDE AND CARBON MONOXIDE FROM POLYIMIDE COMBUSTION

Air flow, cc/min	31	37	69	69
Oxygen flow, cc/min	26	0	0	0
Heating rate, C/min	5	5	5	50
Carbon dioxide*	1682	2037	1788	2005
Carbon monoxide	409	355	565	342
%Plastic accounted for	63.4	75.9	81.1	69.4

*The quantity of each combustion product is reported in milligrams per gram of sample.

Oxides of nitrogen (nitric oxide and nitrogen dioxide) were determined by the Saltzman spectrophotometric method and were found to be present in very low concentrations using the 0-to 1000-C temperature range. Higher temperatures would probably be required to produce significant quantities of nitrogen oxides. Note the trend of nitrogen dioxide to increase with increasing air supply (Table 15). Water and cyanogen elute at the same time on the Porapak Q chromatograph column and other interferences are possible, so this column was not used for quantitative work. Hydrogen cyanide was initially quantitated using a silver nitrate titration in the presence of potassium iodide, leading to an average value of 15 mg cyanide /g. Interference with this titration could not be ruled out and the analyses were repeated using an Orion Cyanide Ion Electrode. With it, 15 to 30 milligrams of cyanide were determined per gram of sample (Table 15). Semiquantitative analysis of benzonitrile indicated about 5 milligrams per gram of sample. Compounds in the liquid residue were not quantitated.

TABLE 15

CYANIDE AND NITROGEN OXIDES FROM POLYIMIDE COMBUSTION

Air flow, cc/min	100	100	475	100
Oxygen flow, cc/min	0	20	0	0
Heating rate, C/min	5	5	5	50
Cyanide ion (as HCN)*	24.3	29.7	21.6	18.9
Nitric oxide (NO)	0.22	0.16	0.48	N.A.†
Nitrogen dioxide (NO_2)	0.20	0.53	0.71	N.A.†

*The quantity of each combustion product is reported in milligrams per gram of sample.

†Not analyzed.

Discussion

Total accounting of polyimide nitrogen was not accomplished, although significant quantities of cyanide and organic nitrogen compounds were found. Nitrous oxide was not quantitated due to technical problems, but it is the oxide of nitrogen most likely to be present under our combustion conditions. Experience with other plastics, particularly Lopac^R and Barex^R, has shown that molecular nitrogen may well be a combustion product of nitrogen-containing polymers, although it would not be detected in the presence of air. As explained in the section on polyurethanes, the combination of carbon monoxide and hydrogen cyanide is particularly hazardous in accidental combustion.

LOPAC^R

Introduction

Lopac^R is a new plastic developed for beverage bottles and is reported to be a methacrylonitrile-styrene copolymer. According to M. F. Gigliotti of Monsanto, Lopac's^R manufacturer, "When incinerated the containers behave like wood or proteins both mechanically and chemically."[29]

Sample

Lopac^R bottles were obtained from the manufacturer. They were found by analysis to be composed of 18.8 percent nitrogen.

Results

Thermal analysis. Lopac^R was analyzed by differential thermal analysis in both helium and air atmospheres (Figure 26). Its decomposition on slow heating was entirely endothermic, peaking at 405 C in helium and 375 C in air. Smaller endothermic peaks appear at 335 C in helium and 325 C in air. Lopac^R is the only plastic analyzed by DTA in this study which did not show any exothermic reaction in the air. Thermogravimetric analysis in air (Figure 27) showed a single degradation step between 300 and 415 C, although there may be a slight inflection (not detectable in the figure) at 375 C. Thermal data indicate degradation occurs primarily by depolymerization.

Qualitative analysis. Infrared analysis of Lopac^R combustion gas (Figure 28) in a 10-cm path-length cell showed bands due to C-H groups, carbon dioxide, carbon monoxide, methacrylonitrile, and cyanide. Analysis of Lopac^R gaseous products by GC-MS showed two major compounds, methacrylonitrile and styrene. The large amount of condensed liquid residue left after Lopac^R combustion showed 10 to 15 compounds by GC-MS, the major ones again being methacrylonitrile and styrene. Vinylpyridine, molecular weight 105, was also present. Remaining gaseous and liquid products have not yet been identified.

Quantitative analysis. Only cyanide ion has thus far been quantitated in Lopac^R combustion gas. Table 16 shows cyanide ion concentrations at three combustion conditions. Samples were temperature programmed at the indicated heating rate from 250 to 800 C.

Discussion

Lopac^R has been found by others to be completely combusted to carbon dioxide, water, nitrogen, and a trace of cyanide when incineration conditions are used.[29] However, a variety of compounds including cyanides may be generated under inefficient combustion

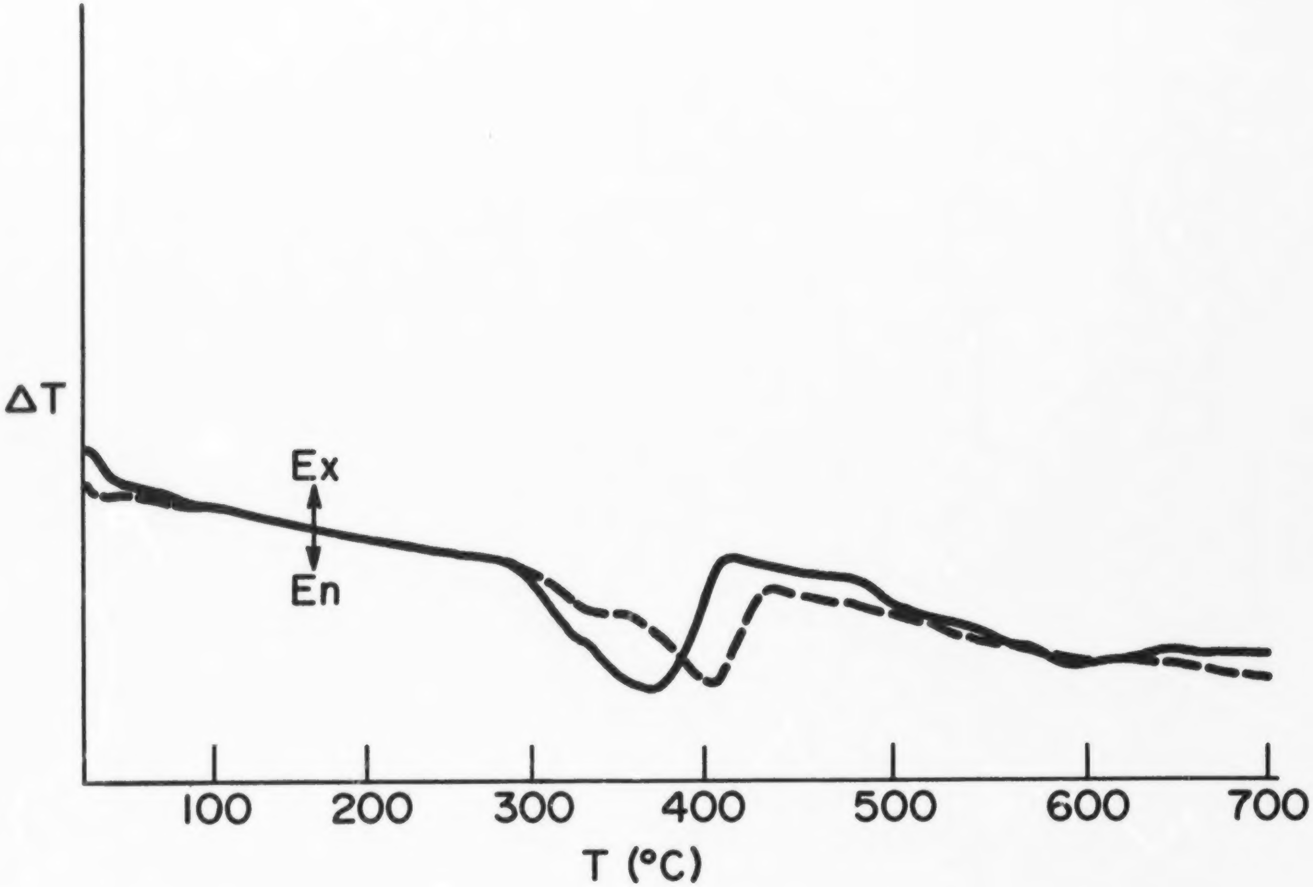


Figure 26. Differential thermal analysis records of Lopac^R heated at 10 C/min in helium (broken curve) and air (smooth curve)

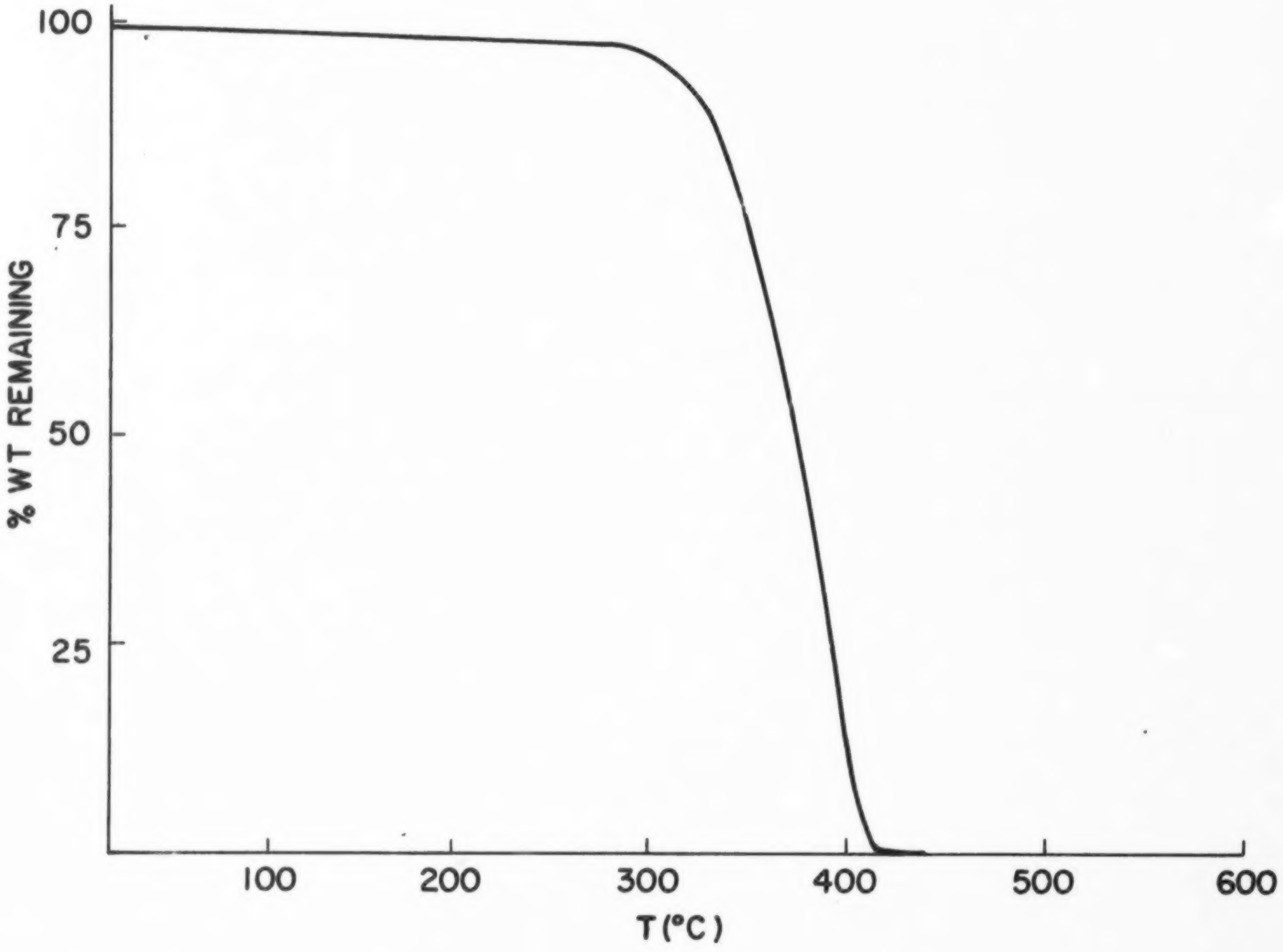


Figure 27. Thermogravimetric analysis record of Lopac^R heated at 10 C/min in air

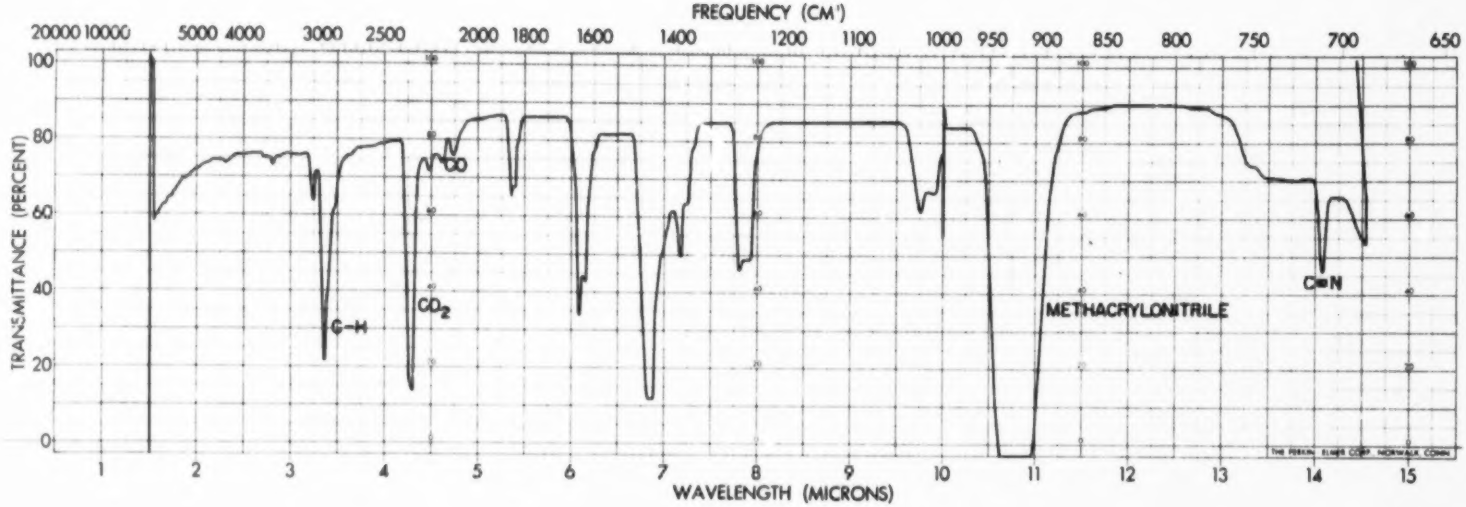


Figure 28. Infrared spectrum of Lopac^R combustion gas (10-cm path-length gas cell)

conditions. The endothermic nature of initial Lopac^R degradation might limit Lopac's^R value in incinerators attempting to recover thermal energy. However, further degradation of the endothermic depolymerization products may be exothermic.

TABLE 16

CYANIDE FROM LOPAC^R COMBUSTION

Air Flow (cc/min)	Oxygen Flow (cc/min)	Heating Rate (C/min)	Cyanide Ion Concentration (mg/g)
100	0	5	6.64
100	20	5	7.54
475	0	50	3.51

BAREX^R

Introduction

Barex^R is another plastic currently being test-marketed for soft-drink bottles. It is manufactured by Vistron Corporation and is reported to be an acrylonitrile-ethyl acetate-butadiene terpolymer. The potential market for plastic soft-drink bottles in general is in the billion bottle-per-year range[3] and, since such bottles would be used once and disposed, their use could have a significant impact on the composition of solid waste.

Sample

The sample studied was Barex^R-210, lot number 758370. It is composed of 17.43 percent nitrogen. Since this plastic is still being developed and tested, significant lot variations would not be surprising.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis of Barex^R in air (Figure 29) shows a multi-step decomposition with only a 3-percent weight loss by 310 C. A rapid 24-percent weight loss occurs between 310 and 327 C and there is a more gradual 26-percent loss between 327 and 450 C. Another 11-percent weight loss occurs very gradually until 600 C, leaving a 36-percent residue at that temperature.

Qualitative analysis. Infrared analysis of Barex^R combustion gas (Figure 30) in a 10-cm path-length cell shows bands due to C-H groups, carbon dioxide, carbon monoxide, methane, ammonia, and cyanide. Other combustion gases were not identified. Barex^R also produces a significant amount of liquid residue which chromatographically shows about fifteen components on a five-foot-long, 1/4-in.-diameter column of 3 percent SE 30 (Figure 31). Tentative identifications of these chromatogram peaks are listed in Table 17. Of these compounds, benzonitrile is certainly present and a methyl pyridine and a dimethylpyridine are strongly indicated, although isomers cannot be ruled out. Deficiencies in the mass spectra obtained make identifications of the other compounds tentative.

Quantitative analysis. Ammonia was the only combustion product quantitated. Using the 100-cc/min air flow and 5-C/min heating rate 26 milligrams of ammonia were produced per gram of sample, while using the same conditions but with 20-cc/min oxygen added, 15 milligrams ammonia were produced per gram of sample.

Discussion

Safe incineration is a major requirement for any plastic beverage

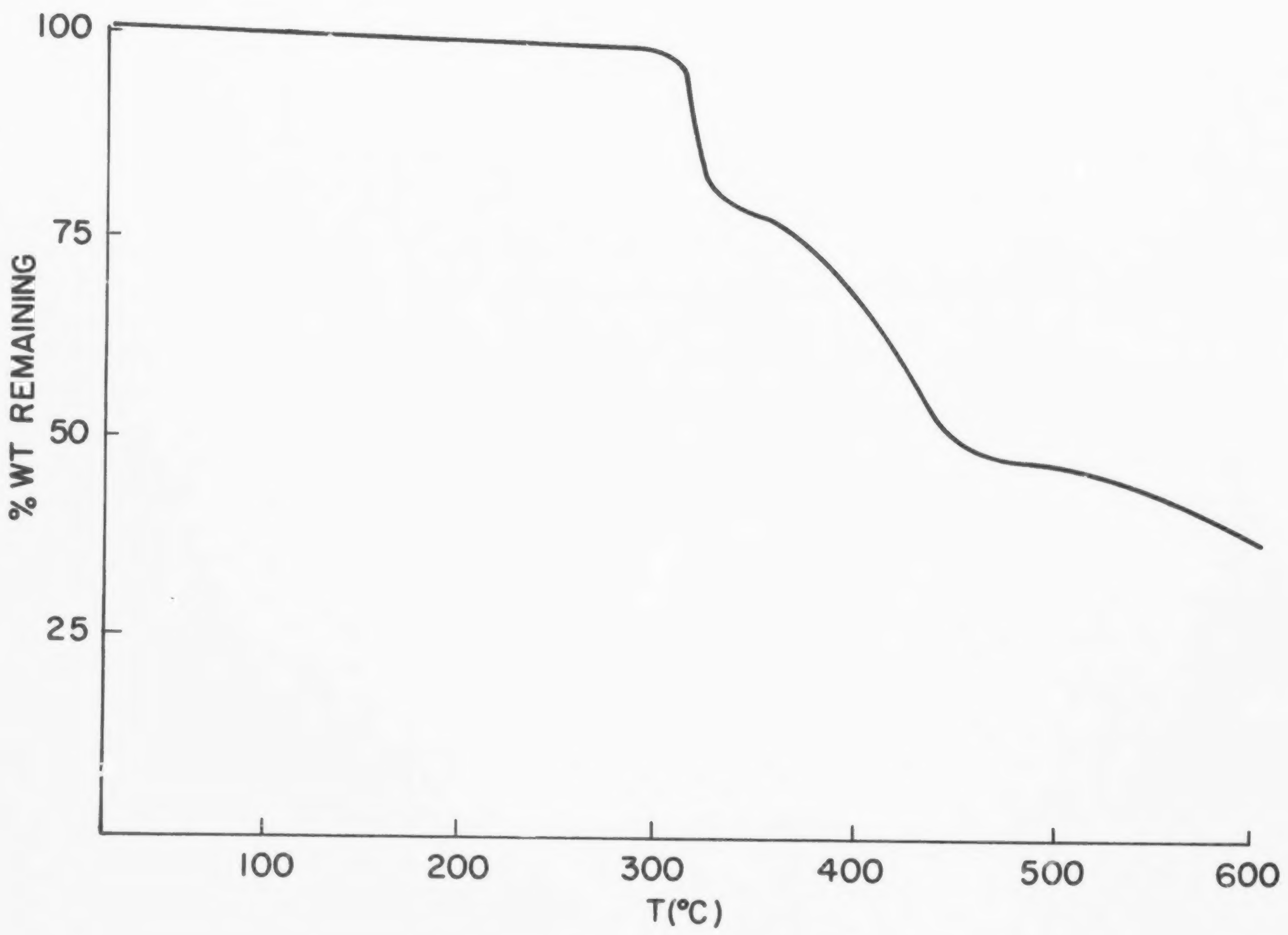


Figure 29. Thermogravimetric analysis record of Barex^R heated at 10 C/min in air

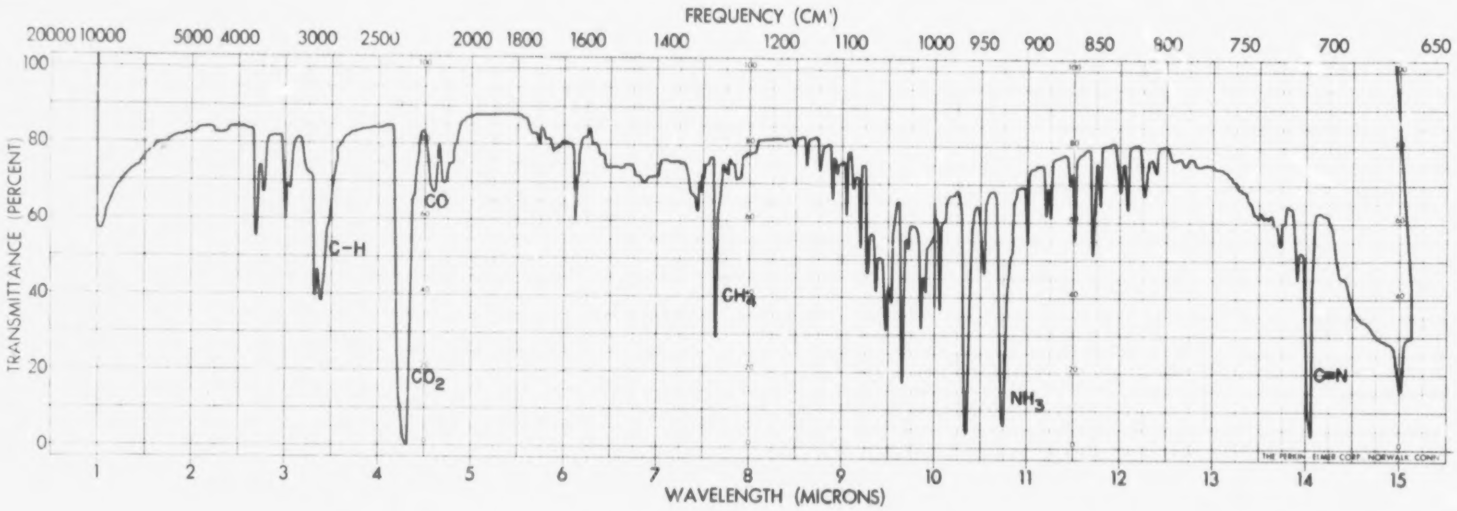


Figure 30. Infrared spectrum of Barex^R combustion gas (10-cm path-length gas cell)

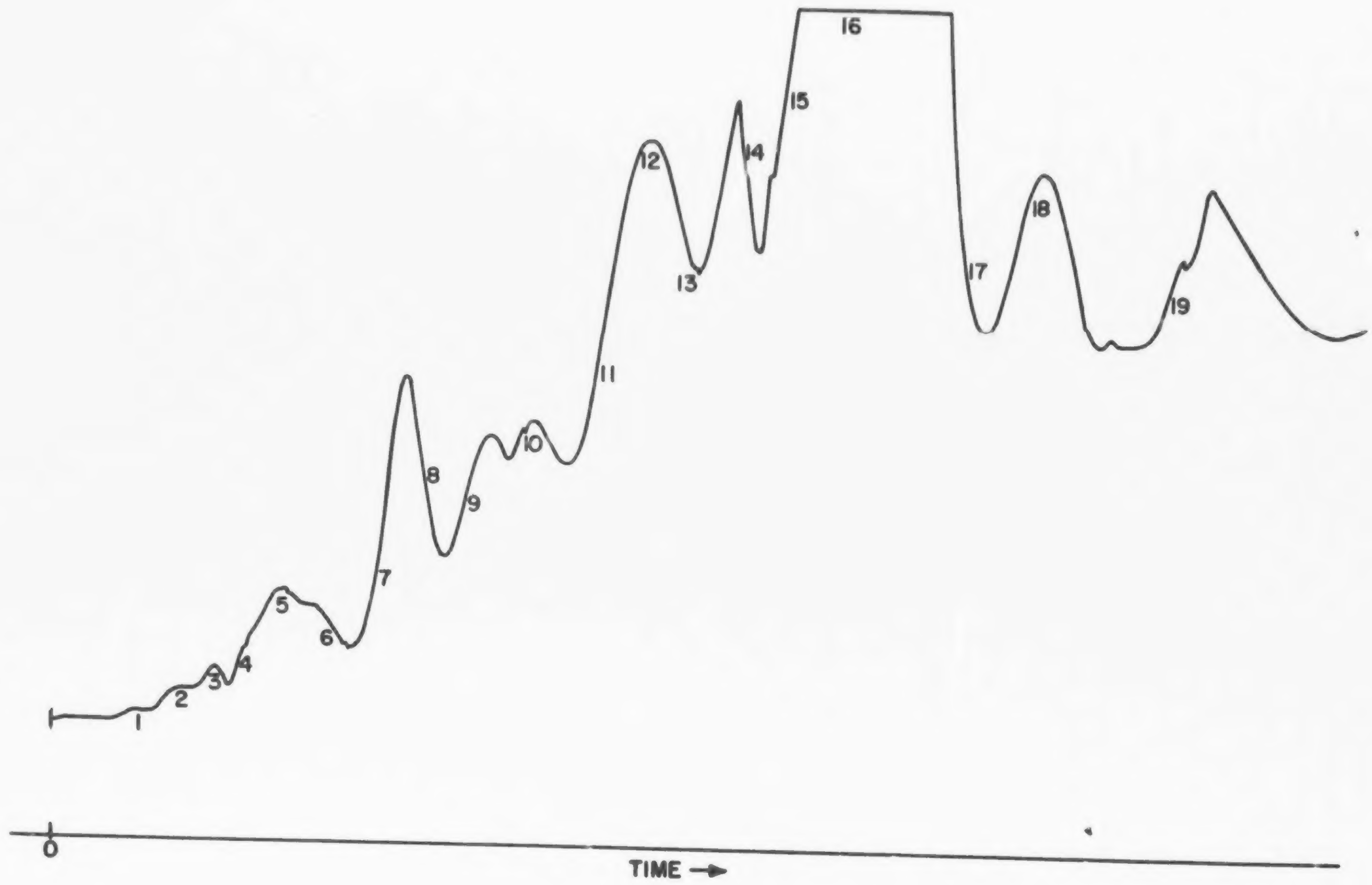


Figure 31. Chromatogram of Barex^R liquid residue on a 3 percent SE 30 column

bottle. The manufacturer of Barex^{R} thus sponsored a study by the Midwest Research Insitute, Kansas City, Missouri[30] in which 0.5 to 8 percent Barex^{R}-210 was added to normal municipal refuse and incinerator stack gases were monitored. Major stack gases were carbon dioxide, water, and nitrogen, with no detectable levels of acrylonitrile, methyl acrylate, acrolein, acrylic acid, or hydrogen cyanide. Properly operated municipal incinerators should completely combust Barex^{R}-210 releasing no undesirable gaseous products. However, the farther removed one gets from proper incineration conditions, the more likely is the generation of hydrogen cyanide and other unidentified products. This is illustrated both by Midwest Research Insitutue's finding of just detectable (0.05 ppm) hydrogen cyanide, slightly increased nitrogen oxides, and methyl acrylate and acrylonitrile on using an apartment-size incinerator and by our own finding of large amounts of products under very unfavorable combustion conditions.

TABLE 17

TENTATIVE IDENTIFICATION OF BAREX^{R} RESIDUE CHROMATOGRAM PEAKS

Peak Number	Molecular Weight	Identification
1	48	Methyl mercaptan?
2	54	Butadiene
3	78	Benzene
4,5,6	74	Propionic acid
	56	Acrolein
7	68	Methylbutadiene*
	55	Ethylcyanide
8	69	Unidentified
9,10	93	Methylpyridine*
11	107	Dimethylpyridine*
	94	Phenol
12,13	103	Benzonitrile
14,15	107	Dimethylpyridine*
16	109	Methoxypyridine*
17	108	Cresol
18	68 or 69	Unidentified
19	117	Methyl cyanobenzene

*Isomer unknown.

UREA FORMALDEHYDE

Introduction

Urea formaldehyde is a thermoplastic resin used for electronic components.

Sample

The sample was a wood-flour-filled urea formaldehyde supplied by Professor R. W. Heimburg and also used in his study of the "Incineration of Plastics Found in Municipal Wastes". It was composed of 23.53 percent nitrogen.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis in air (Figure 32) showed a three-step degradation. Although a 3-percent weight loss occurred before 175 C, the first step was a gradual 11-percent loss between 175 and 260 C. This was followed by a steep 57-percent loss between 270 and 345 C. Above 345 C weight was gradually lost until the plastic was completely combusted at 610 C.

Qualitative analysis. Infrared analysis of urea formaldehyde combustion gas in a 10-cm path-length cell (Figure 33) showed the presence of carbon dioxide, carbon monoxide, methane, ammonia, and cyanide. This sample was run under quite inefficient combustion conditions, producing large quantities of ammonia and cyanide. Other gaseous products were not identified.

Quantitative analysis. Only cyanide ion was quantitated. Using a 100-cc/min air flow and 5-C/min heating rate, 18.9 milligrams cyanide ion were produced per gram of sample.

Discussion

This sample was sent to us by Professor Heimburg because it was particularly toxic to plants and animals when burned using inefficient combustion conditions. His report states[7]: "However, if there was not enough premixing or a high enough afterburner temperature, urea formaldehyde became the most hazardous and corrosive material encountered." His study did not run other nitrogen-containing polymers such as polyurethane or Barex^R under similarly deficient conditions, however. Cyanide and carbon monoxide are the only acutely toxic compounds identified in either of our studies. The fact that animals removed from exposure before death recovered rapidly is evidence for this particular combination of toxicants being responsible for the observed effects.

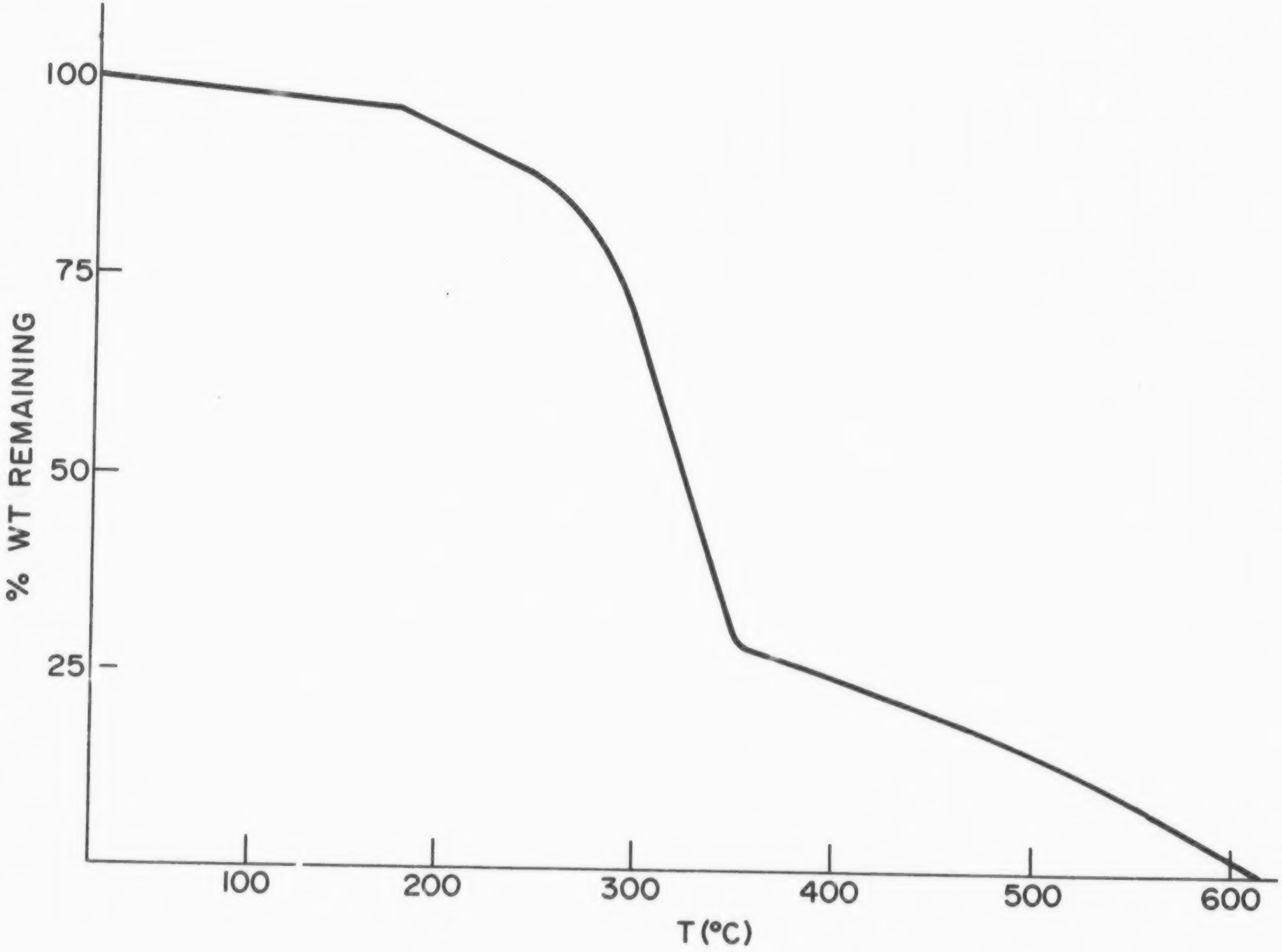


Figure 32. Thermogravimetric analysis record of urea formaldehyde heated at 10 C/min in air

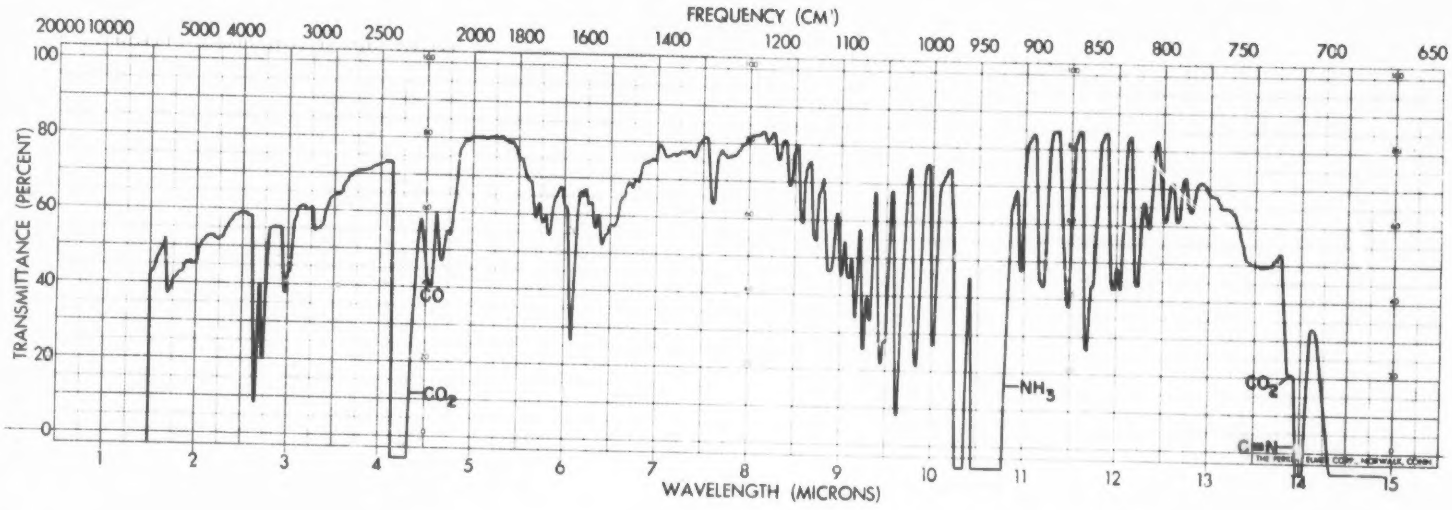


Figure 33. Infrared spectrum of urea formaldehyde combustion gas (10-cm path-length gas cell)

PHENOL FORMALDEHYDE

Introduction

Phenol formaldehyde is a thermoset plastic and is among the older resins now in use. It is used extensively in electrical equipment and many studies of its combustion products have been made, mostly in vacuum. According to Madorsky[5], who quantitated approximately fifteen pyrolysis products at four constant temperatures, the resin is highly cross-linked because formaldehyde can react ortho, meta, or para to the hydroxyl group of phenol.

Sample

The sample tested was a wood-flour-filled Bakelite^R provided by Professor R. W. Heimburg and also used in his study of "Incineration of Plastics Found in Municipal Wastes".[7]

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis in air (Figure 34) showed a multi-step decomposition. There was a gradual 3.5-percent weight loss by 175 C followed by a 20.5-percent loss between 175 and 360 C. There was then a steady weight loss up to 620 C, at which temperature 30.5 percent of the plastic remained uncombusted. Burns & Orrell have found four temperature ranges up to 400 C, where changes, including curing and crosslinking, occur.[31] Shebozake et al have also observed that sample weight may affect the TGA curves of phenol formaldehyde in air.[32]

Qualitative Analysis. Major combustion products of phenol formaldehyde determined by infrared analysis include carbon dioxide, carbon monoxide, methane, and possibly ammonia (Figure 35). Cyanide concentration was below the detection limit of infrared spectrophotometry. Minor combustion products were not identified.

Quantitative analysis. One analysis of phenol formaldehyde products for ammonia was made. Using the 100-cc/min air flow and 5-C/min heating rate, 7.06 milligrams of ammonia were observed per gram of sample. Cyanide ion was also quantitated as indicated in Table 18. The last four values were obtained on a single heating run. Cyanide ion is formed primarily during the early stages of combustion, at the lower temperatures.

Discussion

Professor Heimburg found this plastic produced no ill effects in

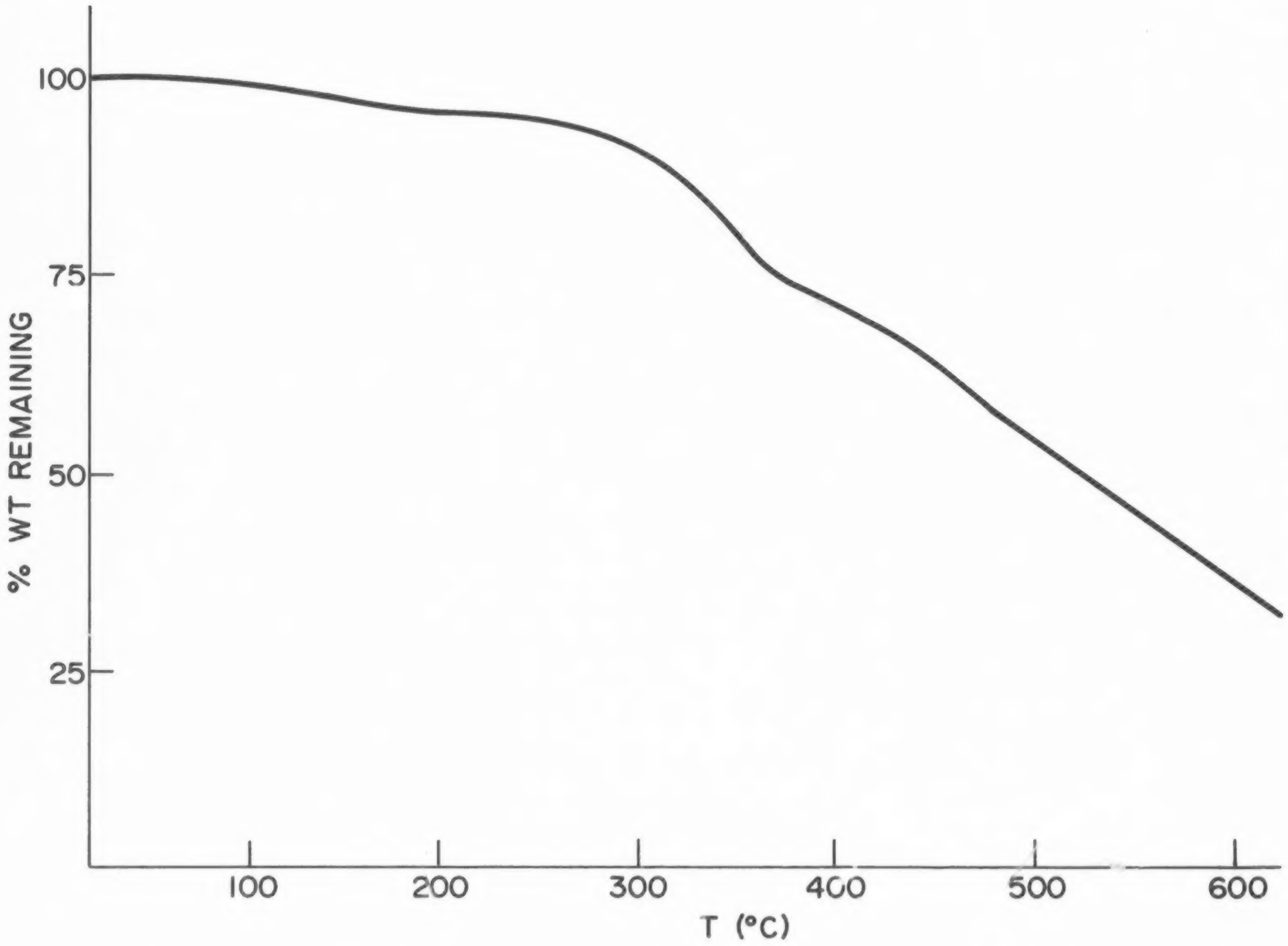


Figure 34. Thermogravimetric analysis record of phenol formaldehyde heated at 10 C/min in air

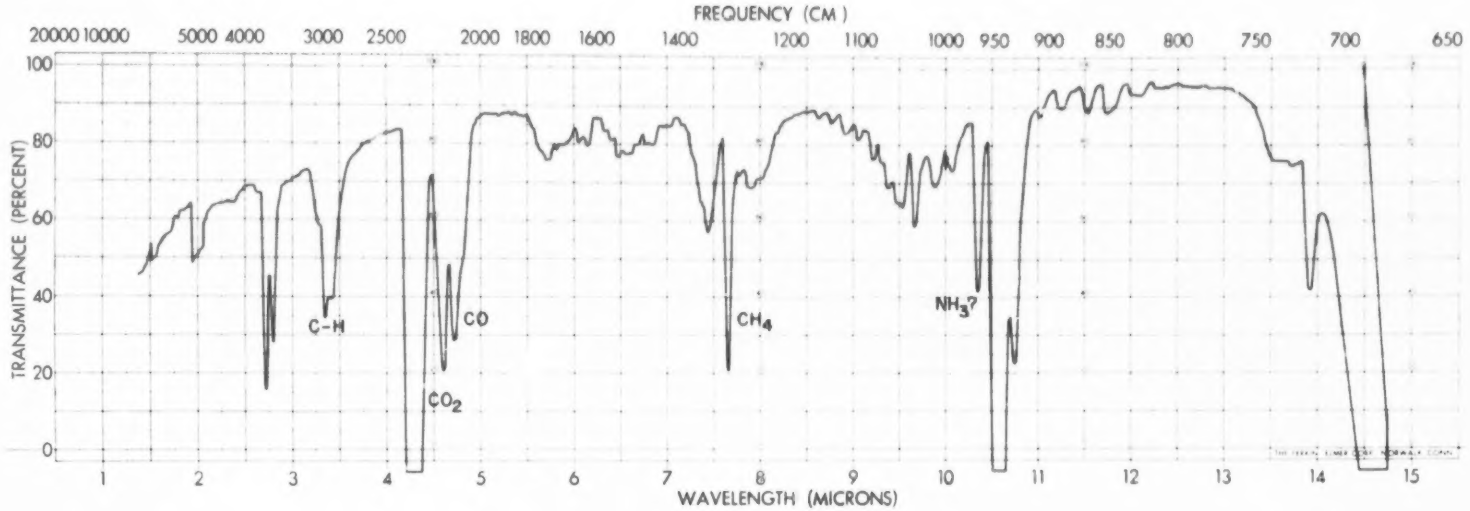


Figure 35. Infrared spectrum of phenol formaldehyde combustion gas (10-cm path-length gas cell)

TABLE 18

CYANIDE FROM PHENOL FORMALDEHYDE COMBUSTION

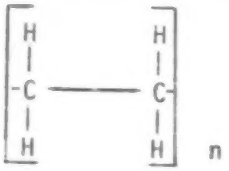
Air Flow (cc/min)	Oxygen Flow (cc/min)	Heating Rate (C/min)	Temperature Range (C)	Cyanide Ion Concentration (mg/g)
100	0	5	0-1000	3.51
100	40	5	0-1000	1.95
100	0	50	0-1000	2.09
100	0	5	0-550	2.09
100	0	5	550-850	1.14
100	0	5	850-1000	0.41
100	0	5	at 1000	0.15

either plants or animals when efficiently combusted. The particular phenol formaldehyde tested can form small amounts of nitrogen compounds. No conclusion as to toxicity can be drawn pending further analytical work.

POLYETHYLENE

Introduction

More polyethylene is produced than any other plastic, with the high- and low-density materials totaling over six billion pounds per year.[4] For this reason and the fact that it is often used for packaging and other disposable goods its volume contribution to solid waste is the largest of all the plastics. Polyethylene consists of 85.7 percent carbon and 14.3 percent hydrogen. Its structure is:



$$\left[-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\overset{H}{\underset{H}{\overset{|}{\underset{|}{C}}}}-\right]_n$$

The high-density material differs from the low-density material in having less branching of the chains. Combusting polyethylene to carbon dioxide and water is not difficult, but incomplete combustion leads to many hydrocarbon products. Madorsky has studied the vacuum pyrolysis of polyethylene.[5]

Samples

Three polyethylene samples were studied: a low-density polyethylene powder, a high-density polyethylene powder, and a high-density polyethylene in pellet form.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis in air of each of the three polyethylene samples (Figures 36 to 38) showed no weight loss until about 325 C with each plastic completely decomposed by 500 to 550 C in a single degradation step. Weight loss of the pellet sample was not as smooth as that of the powder samples initially, perhaps because of temperature gradients within the pellets.

Qualitative analysis. Infrared analysis of polyethylene combustion gas in a 10-cm path-length gas cell showed carbon dioxide, carbon monoxide, and methane to be present along with bands due to C-H, alcohol, and carbonyl groups. Separation of minor products on a six-foot-ling, 1/4-in.-diameter column of Durapak n-Octane/Porasil C and identification by mass spectrometry revealed straight-chain saturated and unsaturated hydrocarbons through C_6. Ethylene, ethane, methanol, and acetaldehyde were separated on a column of Porapak Q of the same dimensions as the Durapak column. Analysis of the liquid residue left after polyethylene combustion by GC-MS

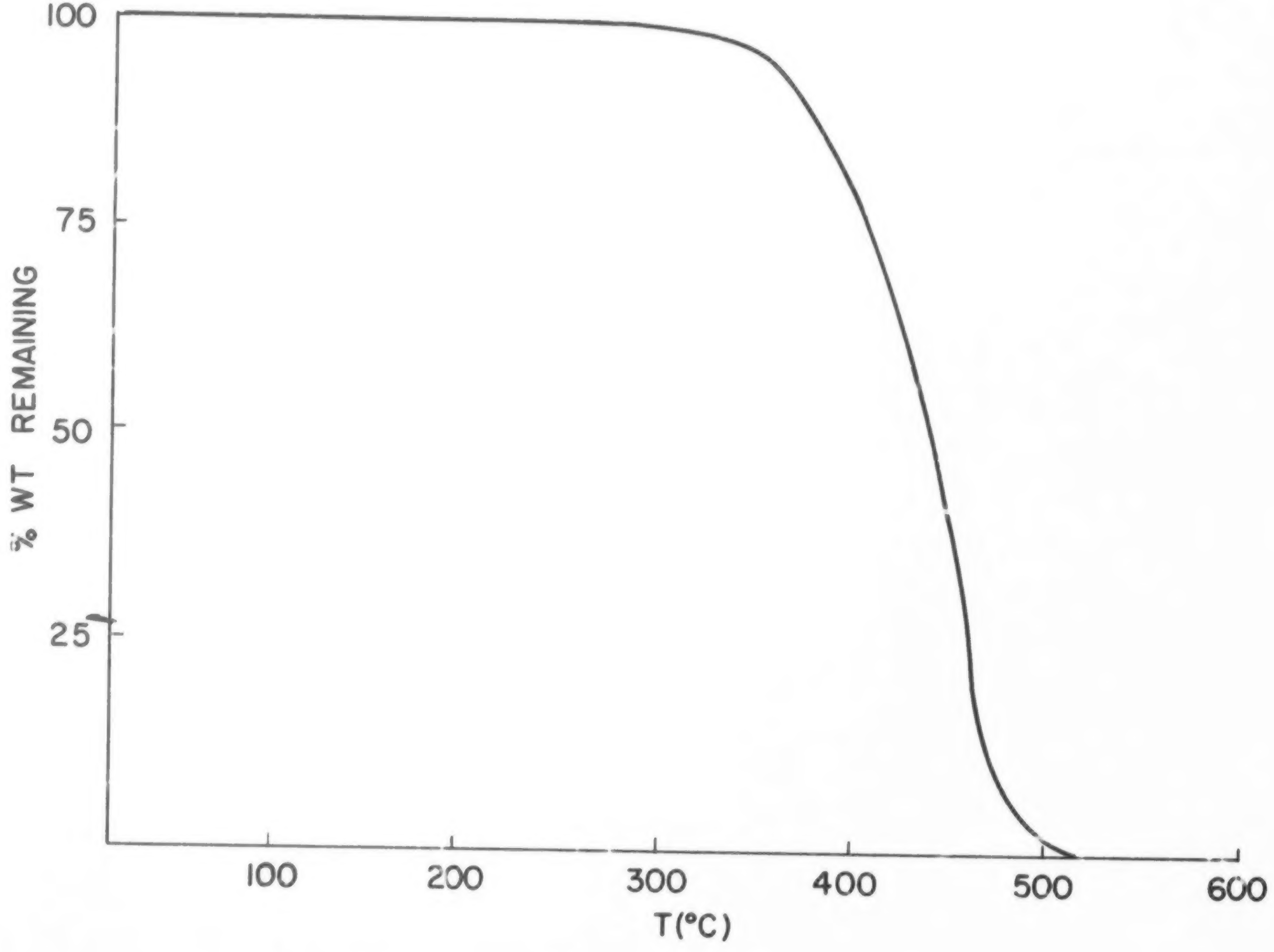


Figure 36. Thermogravimetric analysis record of low-density polyethylene (powder) heated at 10 C/min in air

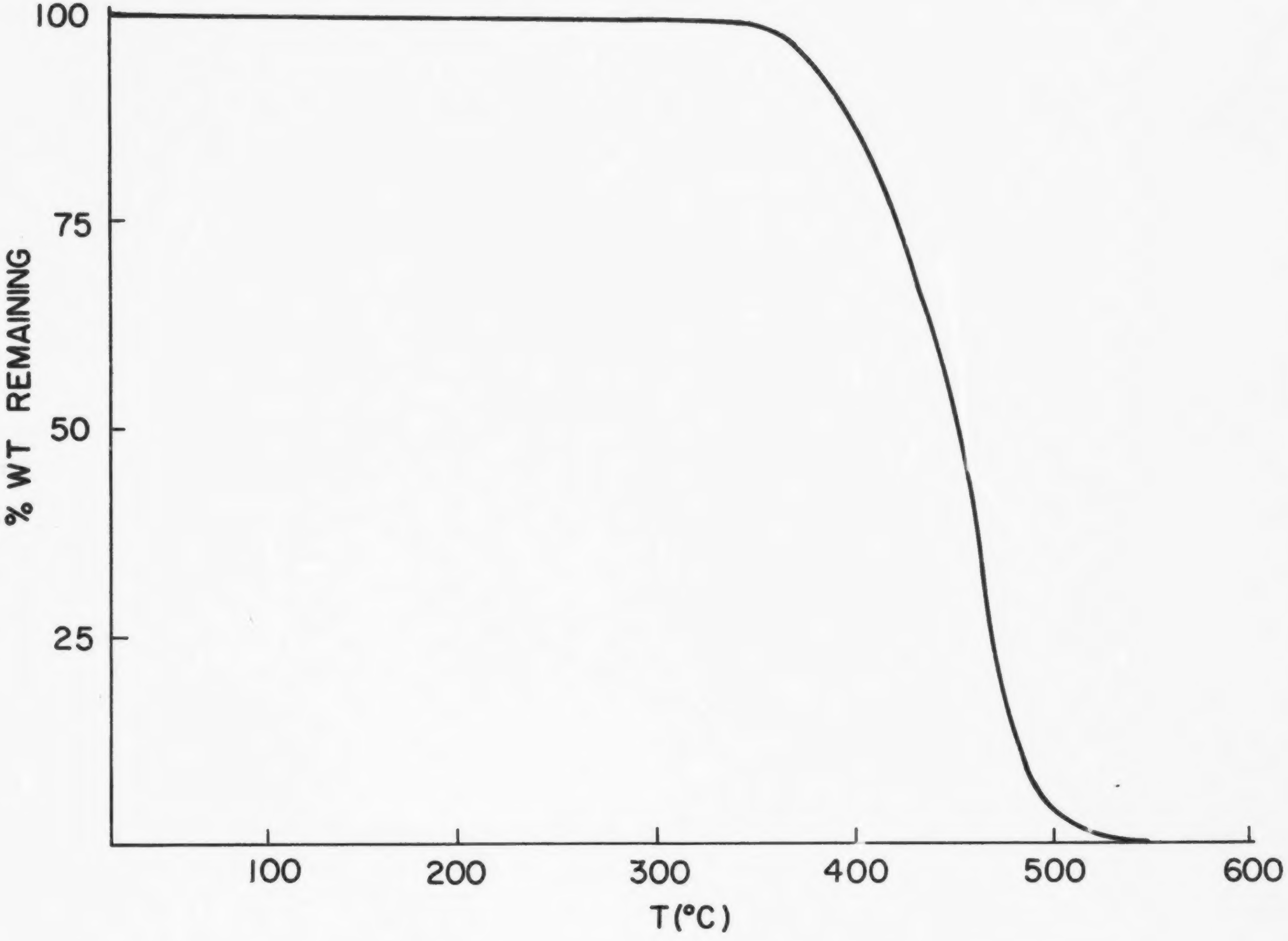


Figure 37. Thermogravimetric analysis record of high-density polyethylene (powder) heated at 10 C/min in air

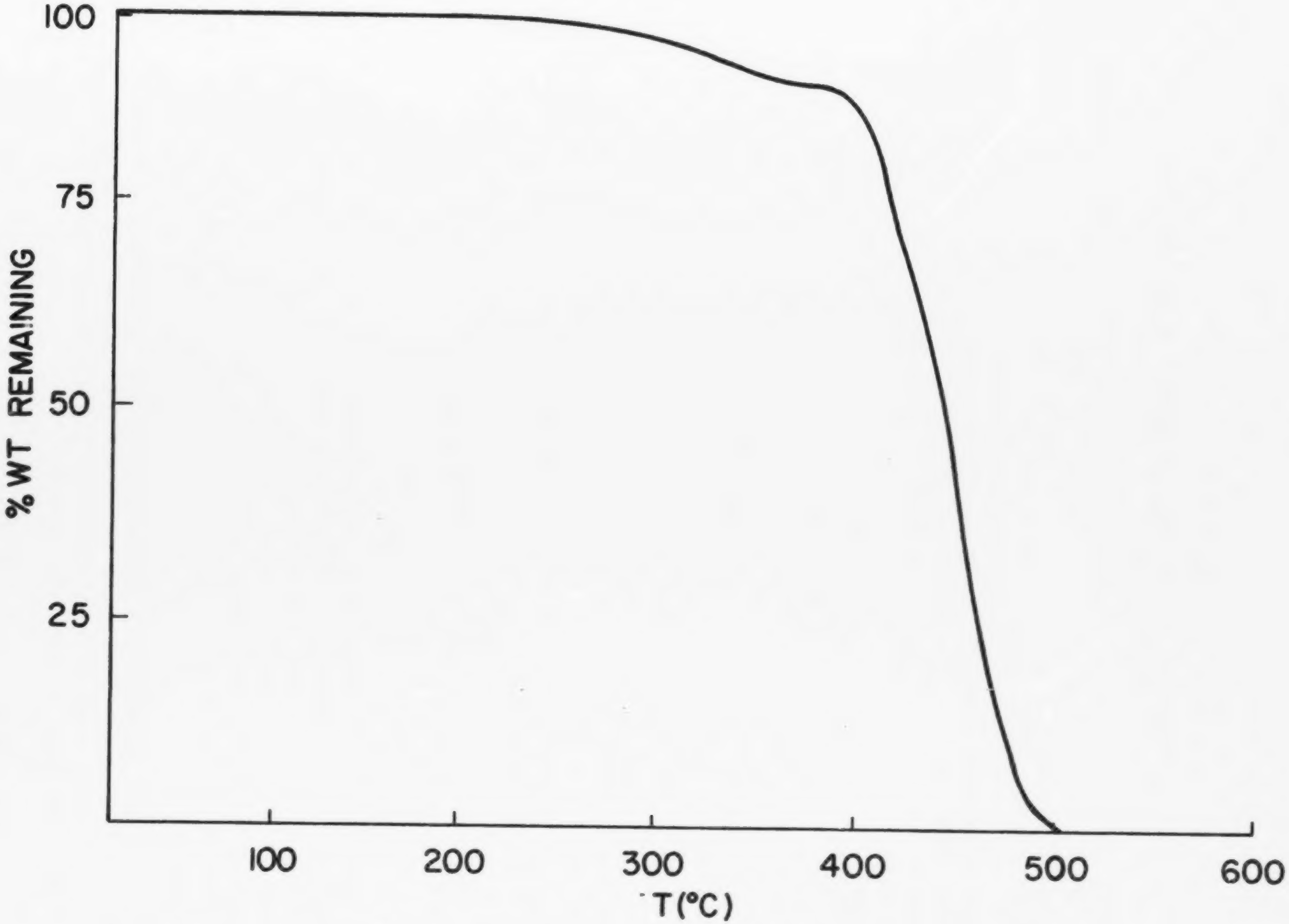


Figure 38. Thermogravimetric analysis record of high-density polyethylene (pellets) heated at 10 C/min in air

TABLE 19

COMBUSTION PRODUCTS OF LOW-DENSITY POLYETHYLENE (POWDER) AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	88.	1610.	178.
Carbon monoxide	312.	171.	110.
Methane	10.4	6.82	16.8
Ethylene	39.6	33.4	70.4
Ethane	4.65	2.83	11.2
Propylene	29.4	14.0	33.1
Propane	5.06	2.58	7.25
1-Butene	16.7	7.65	19.0
Butane	4.15	2.35	6.45
trans-2-Butene	5.68	4.23	9.0
cis-2-Butene	0.95	0.50	1.41
1-Pentene	9.13	4.30	11.8
Pentane	2.28	1.06	3.35
1,3-Pentadiene?	23.0	8.44	32.0
1-Hexene	10.0	4.92	14.7
2-Hexene	4.11	2.04	5.72
%Plastic accounted for	32.3	60.7	33.8

*The quantity of each combustion product is reported in milligrams per gram of sample.

using a five-foot-long, 1/4-in.-diameter column of low K' Durapak resulted in a chromatogram composed of about ten peaks spaced in a pattern characteristic of a homologous series of compounds. Chromatographic retention times of the peaks matched well with those of C_8-to C_{24}-saturated hydrocarbons, but identifications could not be made by mass spectrometry because the molecular ions, and thus the molecular weights of the compounds, could not be determined. Molecular ions of hydrocarbons often do not appear in mass spectra, as they are very much less likely to form than fragmentation ions. A homologous series of unsaturated hydrocarbons would actually seem more likely to form than one of saturated hydrocarbons from polyethylene combustion.

Quantitative analysis. Carbon dioxide and carbon monoxide were quantitated by infrared spectrophotometry. Most of the hydrocarbon products were quantitated by gas chromatography on the same columns

TABLE 20

COMBUSTION PRODUCTS OF HIGH-DENSITY POLYETHYLENE (POWDER) AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	129.	753.	203.
Carbon monoxide	261.	179.	123.
Methane	15.2	7.75	17.7
Ethylene	32.6	31.0	49.6
Ethane	3.55	1.69	10.8
Propylene	37.7	20.4	37.2
Propane	4.92	1.92	8.5
1-Butene	18.7	9.79	18.5
Butane	3.21	1.44	4.51
trans-2-Butene	7.27	2.70	10.8
cis-2-Butene	1.08	0.54	1.58
1-Pentene	10.8	4.51	13.1
Pentane	2.04	0.72	2.85
1,3-Pentadiene?	25.3	9.25	38.2
1-Hexene	11.2	3.96	16.5
2-Hexene	3.82	1.44	5.52
%Plastic accounted for	32.4	37.9	34.3

*The quantity of each combustion product is reported in milligrams per gram of sample.

used for their separation. Methanol and acetaldehyde were not quantitated. Quantitative results on seventeen combustion products of each of the three polyethylene samples are listed in Tables 19 through 21. Thirty to sixty-five percent of the plastic combusted can be accounted for by the identified products, with the amount accounted for depending strongly on the amount of carbon dioxide produced. Unsaturated hydrocarbon products predominate over the saturated products. Interferences by other compounds with the pentadiene peak have not been ruled out. Polyethylene completely decomposed at such low temperatures that quantities of its combustion products varied considerably. Sufficient data for statistical analysis has not yet been obtained.

Discussion

Carbon monoxide was the only acutely toxic combustion product of

TABLE 21

COMBUSTION PRODUCTS OF HIGH-DENSITY POLYETHYLENE (PELLETS) AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	213.	1842.	388.
Carbon monoxide	255.	173.	208.
Methane	13.1	6.09	17.6
Ethylene	49.0	30.5	52.9
Ethane	4.76	1.98	9.86
Propylene	34.8	11.8	35.3
Propane	5.11	1.78	7.69
1-Butene	18.1	5.77	16.0
Butane	3.63	1.33	4.08
trans-2-Butene	7.05	3.90	9.20
cis-2-Butene	1.01	0.43	1.26
1-Pentene	11.1	3.49	11.7
Pentane	2.22	0.84	2.41
1,3-Pentadiene?	28.6	6.32	30.5
1-Hexene	12.4	2.55	16.1
2-Hexene	4.76	1.20	5.15
%Plastic accounted for	36.3	65.4	41.5

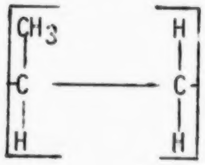
*The quantity of each combustion product is reported in milligrams per gram of sample.

polyethylene identified. The fuel or crude chemical value of the liquid residue, however, should be of primary interest in solid waste management. Under pyrolytic conditions, up to 90-percent yields of the liquid residue can be obtained.

POLYPROPYLENE

Introduction

Polypropylene ranks fourth in the production of plastics with over a billion pounds produced in 1971.[4] Much of the polypropylene produced is used for disposable or short-term-use goods, thus contributing to the total solid waste problem. Polypropylene is composed of 85.7 percent carbon and 14.3 percent hydrogen. Its formula is:



$$\left[-\overset{\overset{CH_3}{|}}{\underset{\underset{H}{|}}{C}}-\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}-\right]$$

On complete combustion polypropylene would be expected to produce only carbon dioxide and water. However, primary burning, open burning, and inefficient incineration could result in production of a variety of hydrocarbons. Madorsky has studied the pyrolysis products of polypropylene.[5]

Sample

The sample studied was an isotactic (all methyls on the same side of the carbon chain) polypropylene powder purchased from Cellomer Associates, Inc., Webster, New York.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis of polypropylene in air (Figure 39) showed a one-step degradation with the plastic completely combusted by 440 C. Polypropylene begins breaking down at a lower temperature than polyethylene because, according to Madorsky[5], alternate carbons in the chain are tertiary making all the C-C bonds weaker.

Qualitative analysis. Carbon dioxide and carbon monoxide were positively identified while methane and propylene were tentatively identified by infrared analysis of polypropylene combustion gas using a 10-cm path-length gas cell. Additional bands due to hydroxyl and carbonyl groups were observed, possibly from methanol, acetone, and/or acetaldehyde. Separation of gaseous products on a six-foot-long, 1/4-in.-diameter Durapak n-Octane/Porasil C column followed by mass spectrometry showed a complete spectrum of C_1- through C_6-hydrocarbons. Much of the polypropylene combusted formed high-boiling liquid residue which has not yet been analyzed.

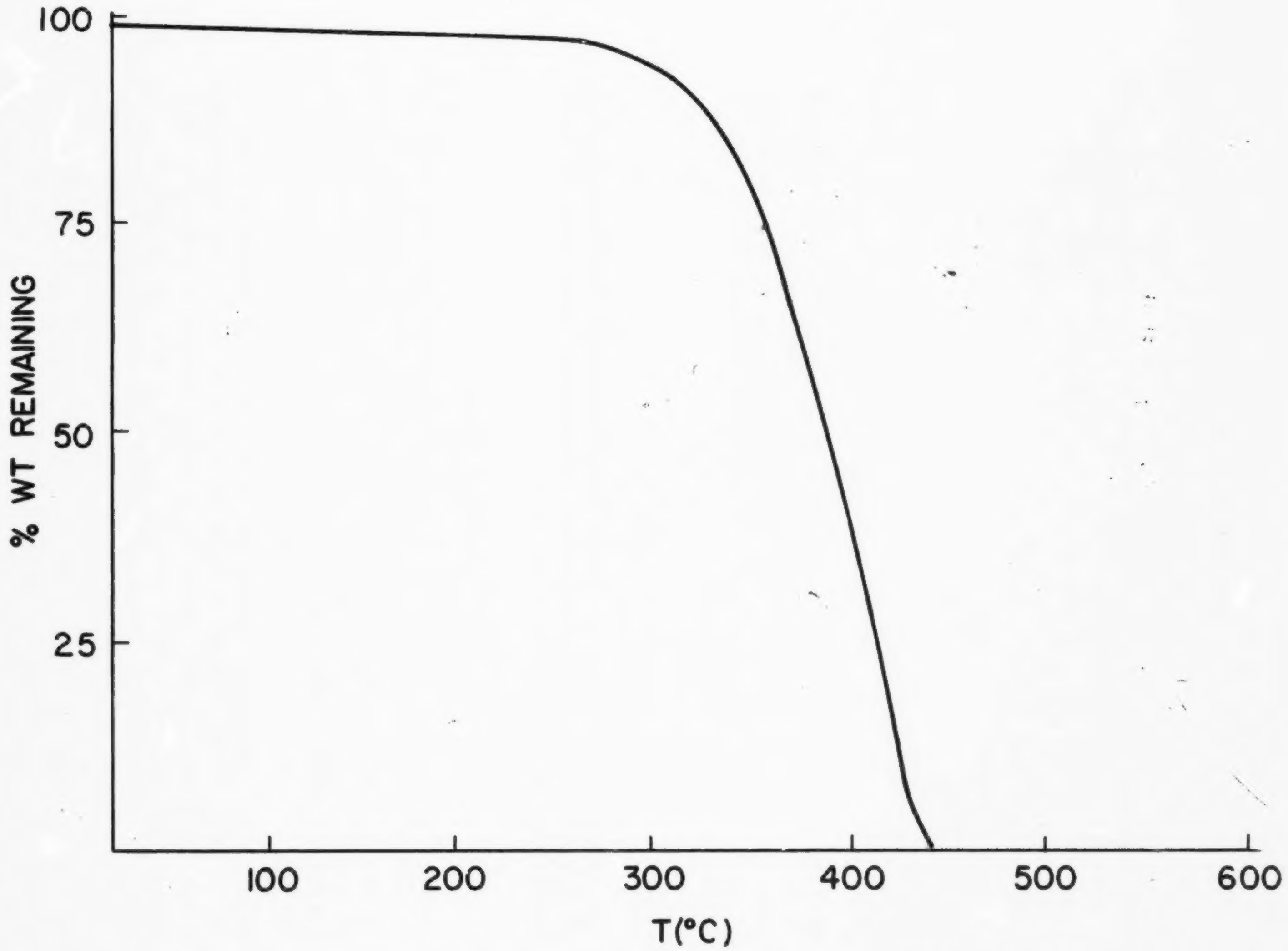


Figure 39. Thermogravimetric analysis record of isotactic polypropylene heated at 10 C/min in air

TABLE 22

COMBUSTION PRODUCTS OF ISOTACTIC POLYPROPYLENE AT SEVERAL COMBUSTION CONDITIONS

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	131.	1195.	284.
Carbon monoxide	214.	284.	208.
Methane	22.8	25.4	151.
Ethylene	8.47	5.68	26.2
Ethane	0.98	0.46	9.77
Propylene	81.0	21.2	314.
Propane	2.00	0.54	7.60
1-Butene	1.37	0.47	4.97
Butane	0.16	0.15	0.67
trans-2-Butene	7.12	2.63	30.4
cis-2-Butene	0.50	0.39	1.15
1-Pentene	2.30	0.31	4.50
Pentane	6.68	0.97	31.6
1,3-Pentadiene?	27.6	5.6	86.0
1-Hexene	12.0	1.70	34.4
%Plastic accounted for	30.0	51.3	86.9

*The quantity of each combustion product is reported in milligrams per gram of sample.

Quantitative analysis. Available quantitative data on polypropylene are listed in Table 22. These data represent single combustion runs so it is not possible to comment on their reproducibility. Exceptionally large quantities of unsaturated hydrocarbons were produced, particularly on fast burning. This may be due to the low temperature at which polypropylene decomposes. Madorsky found many of the same compounds on vacuum pyrolysis but in somewhat different relative amounts.[5]

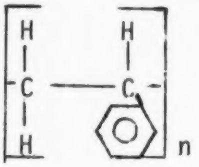
Discussion

Liquid residue from polypropylene combustion has some fuel value which should be utilized. Combustion products thus far identified are of low toxicity, except for carbon monoxide.

POLYSTYRENE

Introduction

Polystyrene is used a great deal for packaging and disposable goods and contributes significantly to the plastics found in solid waste. It is composed of 92.3 percent carbon and 7.7 percent hydrogen, and has the following formula:



Its products of combustion have been studied in vacuum by Madorsky[5], and it has been found that in vacuum styrene accounts for about 75 percent of the polymer degraded. With respect to incineration, more emphasis has been placed on studying soot generation by polystyrene than on identifying gaseous products. Soot generation is a fairly serious problem with aromatic polymers.

Sample

One polystyrene powder sample was obtained from Cellomer Associates, Inc., Webster, New York.

Results

Thermal analysis. Differential thermal analysis was not performed. Thermogravimetric analysis of polystyrene (Figure 40) showed a one-step degradation beginning just before 300 C with the plastic completely combusted at about 450 C.

Qualitative analysis. Separation of polystyrene combustion products on a six-foot-long, 1/4-in.-diameter Porapak Q column showed peaks due to methane, ethylene, ethane, propylene, propane, 1-butene, and possibly methanol and acetaldehyde. GC-MS analysis of polystyrene combustion gas using a five-foot-long, 1/4-in.-diameter 3 percent SE 30 column was sufficient to identify benzene, toluene, ethylbenzene, styrene, and two isomers of methylstyrene. Polystyrene liquid residue, a considerable amount of which formed during combustion, was also analyzed by GC-MS using the SE 30 column. Twenty spectra were taken and about fifteen compounds identified (Figure 41 and Table 23).

Quantitative analysis. Quantitative analysis was not done on polystyrene combustion products.

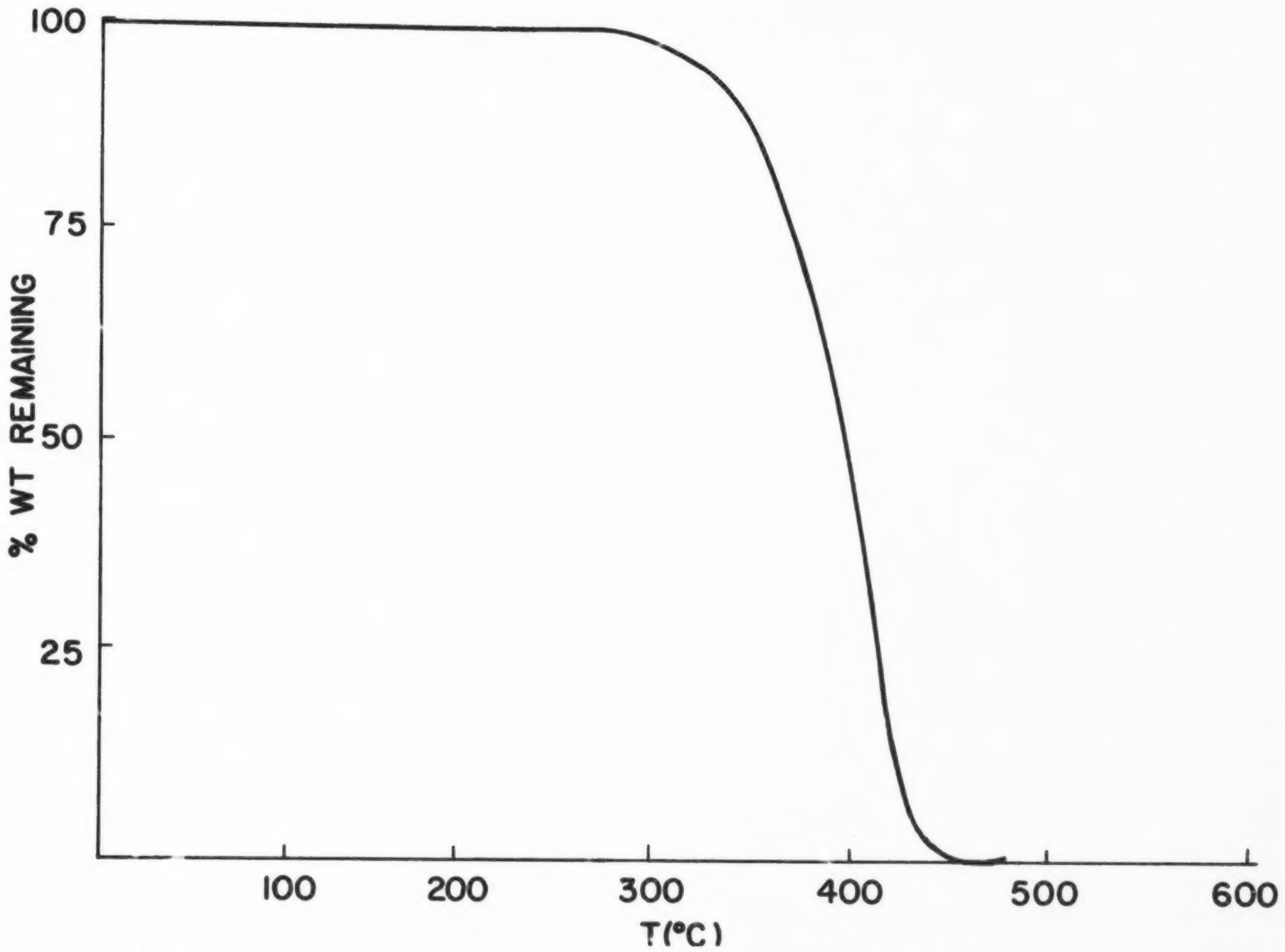


Figure 40. Thermogravimetric analysis record of polystyrene heated at 10 C/min in air

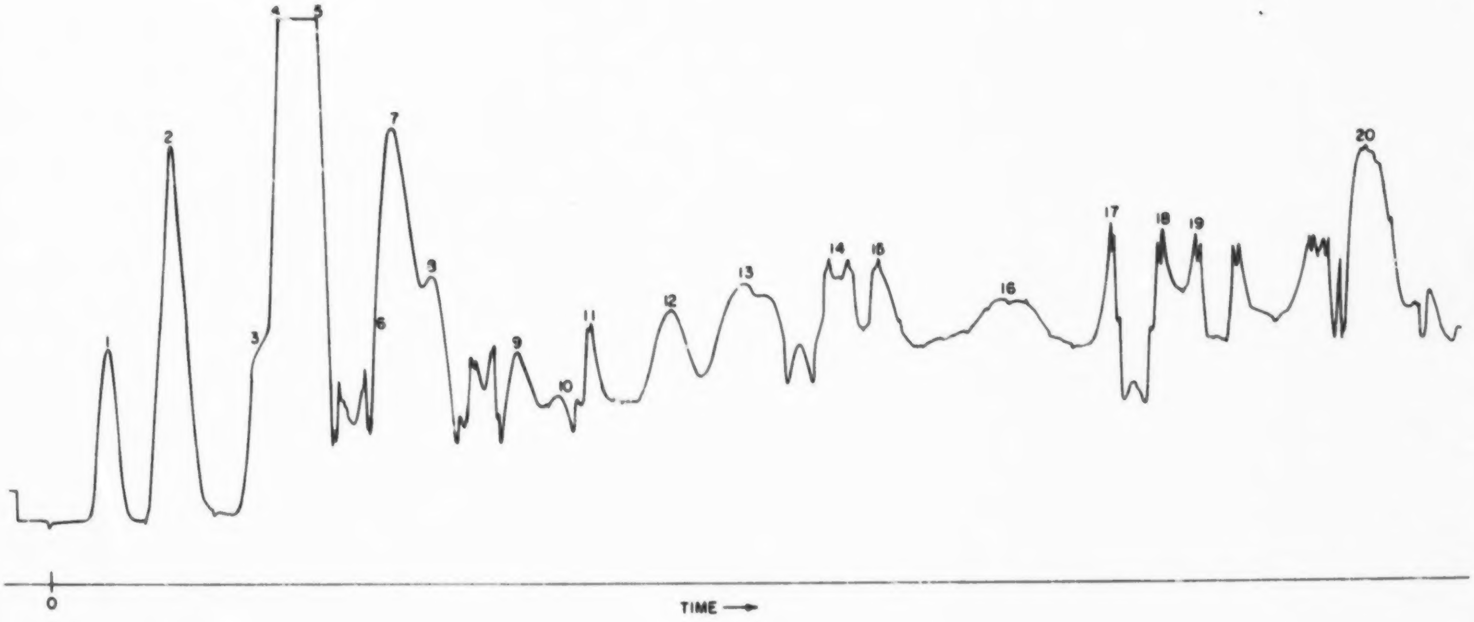


Figure 41. Chromatogram of polystyrene liquid residue on a 3 percent SE 30 column

Discussion

The major component of polystyrene combustion in both the gas and liquid phases is the monomer styrene, although many other compounds are present in significant amounts. There is considerable potential for monomer recovery, as mentioned in a recent TRW report.[33] Aromatic liquid-residue components are chemically quite interesting, as well as potentially toxic.

TABLE 23

IDENTIFICATION OF POLYSTYRENE LIQUID RESIDUE CHROMATOGRAM PEAKS

Peak Number	Molecular Weight	Identification
1	78	Benzene
2	92	Toluene
3	106	Ethylbenzene
4,5	104	Styrene
6	106	Benzaldehyde
	118	Methylstyrene
7	94	Phenol
8	118	Methylstyrene
9	120	n-Propyl benzene
10	116	Indene
11	120	Acetophenone
12	130	Methyl indene
13	---	Unidentified
14	128	Naphthalene
15	134	Cinnamyl alcohol
16	142	Methylnaphthalene
17,18	154	Biphenyl or Acenaphthene
19	168	Methylbiphenyl
20	182	Diphenylethane

POLYCARBONATE

Introduction

Polycarbonate is a specialty thermoplastic developed for its good thermal stability, high strength, and clarity. Its applications include electronic components and window material. Although not a high-production plastic, its combustion products are of interest because they contribute to the overall solid waste disposal problem and also to the toxicity of combustion products during accidental fires in buildings or aircraft. The formula of bisphenol A-polycarbonate, shown in Figure 42, consists of 75.58 percent carbon, 5.55 percent hydrogen and 18.87 percent oxygen.

Samples

Three polycarbonate samples in commercial pellet form were studied.

Results

Thermal analysis. Differential thermal analysis records in helium and in air of one polycarbonate sample are shown in Figure 43. Although this plastic melts in a combustion furnace at about 370 C, no melting endotherms are evident. Small endotherms at 475 C are the first significant features of the DTA records, followed by much stronger endotherms at 520 C. Many volatile and high-boiling products can be collected at temperatures corresponding to these two endotherms. Above 520 C, the reactions are strongly exothermic in air, due in part to formation of carbon monoxide and carbon dioxide, and less strongly exothermic in helium. DTA records of the other two polycarbonate samples were similar to the one shown, except for weaker 520-C endotherms in air.

Thermogravimetric analysis records of another polycarbonate sample are shown in Figure 44. In helium, a one-step degradation is observed with a 75-percent weight loss between 420 and 520 C. The plastic also begins to break down at 420 C in air, losing approximately 55 percent of its weight by 480 C. Another 17 percent of the weight is lost more gradually between 480 and 545 C, with the remaining 28 percent being lost by 600 C. Thus, the 75-percent weight loss occurring in one step in helium, occurs in two steps in air, indicating somewhat different reaction mechanisms.

Several studies of the mechanism of degradation of polycarbonate have been published. Davis and Golden have shown that thermal degradation in vacuo occurs by random chain scission[34], and if volatile products are continuously removed, the polymer is rapidly crosslinked to form a gel.[35] Lee has proposed schemes for the decomposition based on products identified at 475 C under vacuum and in air, but pointed out that above 450 C a complicated mixture

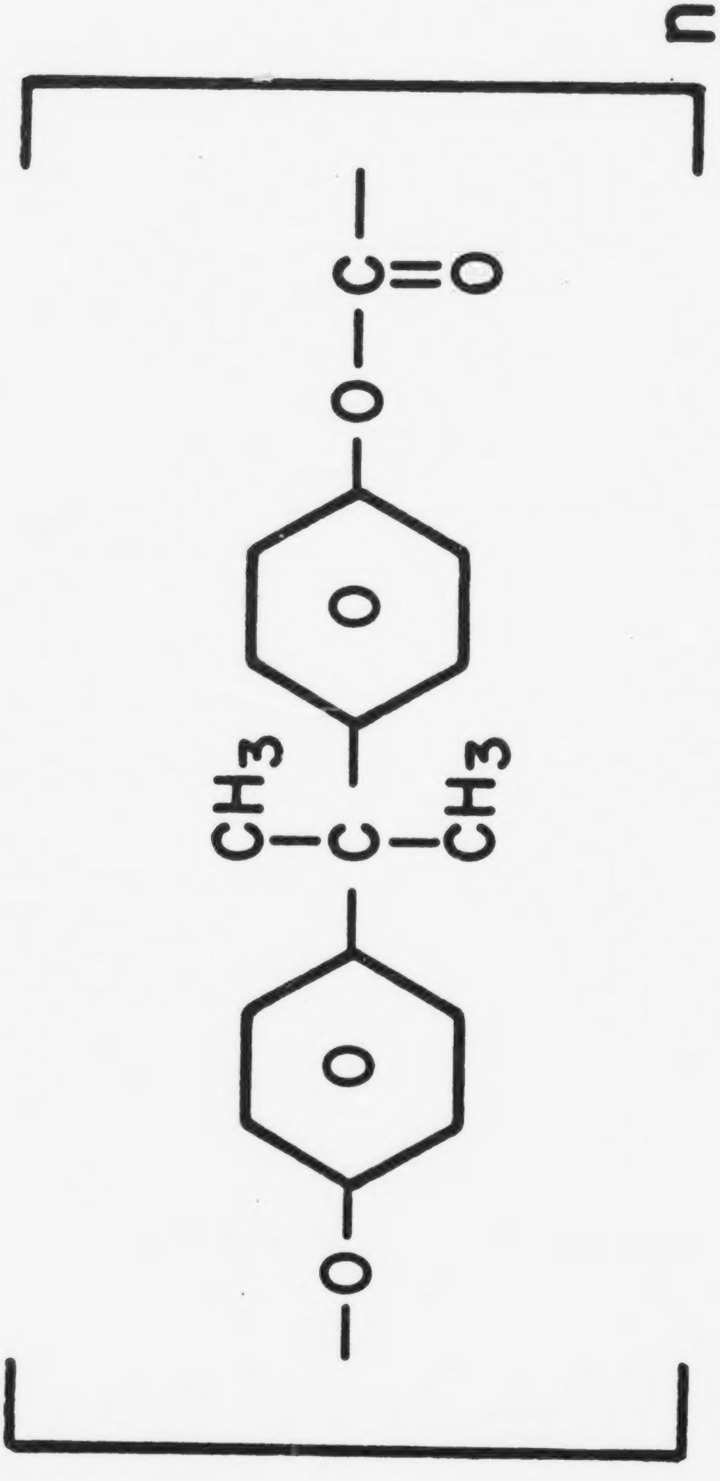


Figure 42. Bisphenol A-polycarbonate

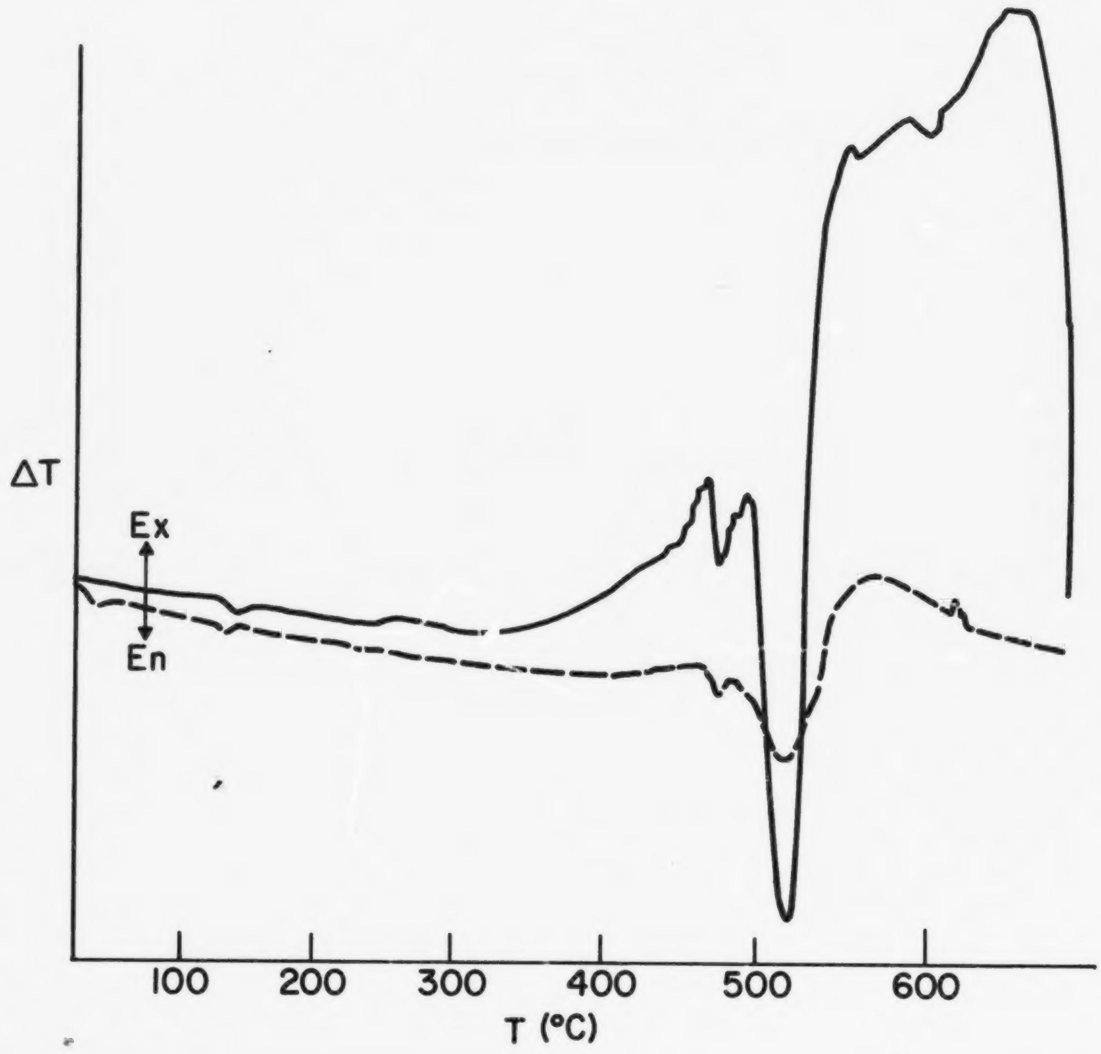


Figure 43. Differential thermal analysis records of polycarbonate heated at 10 C/min in helium (broken curve) and air (smooth curve)

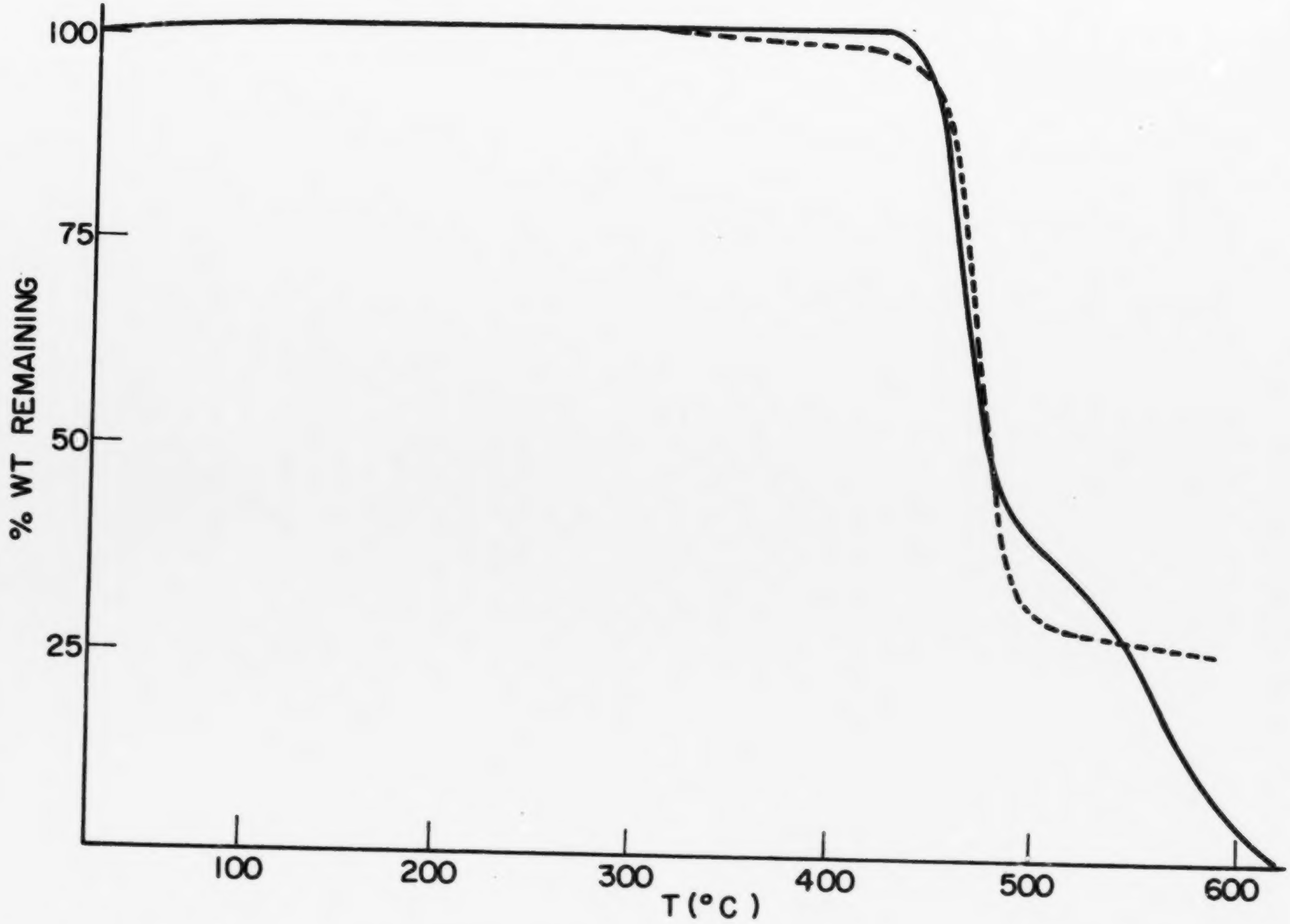


Figure 44. Thermogravimetric analysis records of polycarbonate heated at 5 C/min in helium (broken curve) and air (smooth curve)

of reactions is rapidly taking place.[36]

Qualitative analysis. Gaseous combustion products of polycarbonate were separated on a six-foot long, 1/4-in.-diameter Porapak Q column and on a 13-foot-long, 1/4-in.-diameter column of 5 percent Squalane on Chromosorb P. The former column separated C_1 through C_4 hydrocarbons, methanol, and acetaldehyde. The latter column separated benzene, toluene, ethylbenzene, and styrene. These volatile products along with carbon monoxide and carbon dioxide, which were identified by infrared spectroscopy, account for 40 to 60 percent of the polycarbonate combusted. The remainder of the plastic is accounted for as liquid residue, some components of which were identified using the GC-MS system with a 13-in.-long, 1/4-in.-diameter low K'Durapak column. A chromatogram of polycarbonate products on this column (Figure 45), shows about thirty compounds, many of which are identified in Table 24. Peaks 18-28 were observed on the mass spectrometer total ion current monitor as they were present in large enough quantities to produce off-scale peaks. Although quantitative work was not done on the residue, phenol and substituted phenols seem to predominate. Lee has identified some of the higher-boiling compounds, including isopropenylphenol, isopropylphenol, diphenyl carbonate, and bisphenol A.[36]

Quantitative analysis. During the study of polycarbonate a modification of the combustion furnace temperature controller changed the temperature range from 0 to 800 C to 0 to 1000 C. Polycarbonate data using both temperature ranges are thus available, although most of the study was done using the expanded range. In all cases the temperature was programmed at 5-to 50-C/minute after initial rapid heating from room temperature to 350 C. Table 25 lists 0-to 800-C data for one sample while Table 26 lists data for the three polycarbonate samples using the 0-to 1000-C temperature range. Data at the 5-C/min and 50-C/min heating rates with a 100-cc/min air supply can be compared for the two temperature ranges. The narrower range results in approximately the same amount of carbon dioxide, but much more carbon monoxide and slightly less residue. About two-thirds of the hydrocarbon values are comparable for the two ranges, methane and benzene showing the largest deviations.

Although there appear to be trends within each temperature range which can be explained on the basis of combustion efficiency, these trends do not seem to hold between temperature ranges. For example, at 5 C/min, results for the 0-to 800-C range indicate that as the oxygen supply increases, quantities of carbon dioxide and carbon monoxide increase and the amount of liquid residue decreases. For the 0-to 1000-C range, however, there is more residue and more carbon monoxide at the higher oxygen supply but less carbon dioxide, indicating less efficient combustion, as

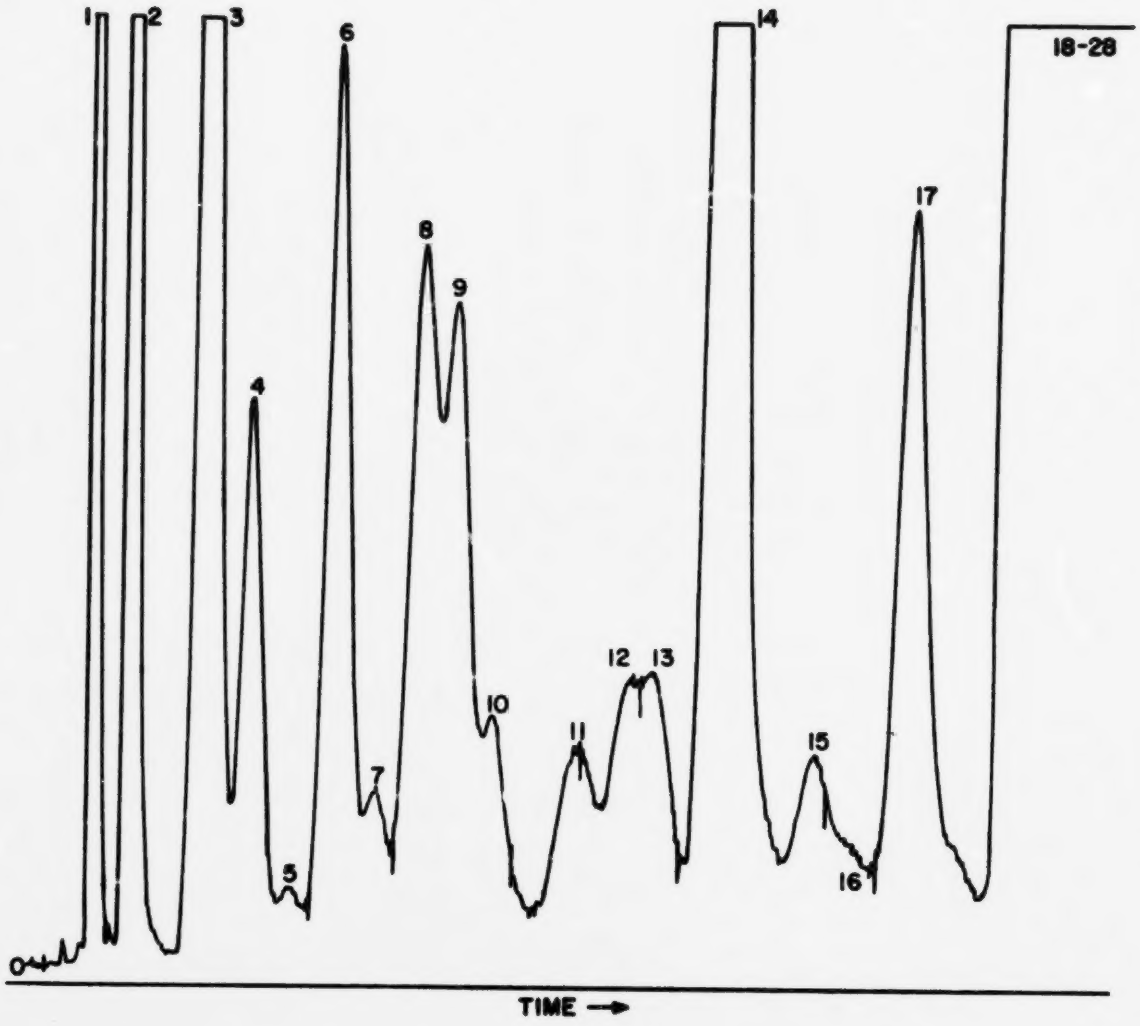


Figure 45. Chromatogram of polycarbonate liquid residue on a low K' Durapak column

TABLE 24

IDENTIFICATION OF POLYCARBONATE RESIDUE CHROMATOGRAM PEAKS

Peak Number	Molecular Weight	Identification
1	78	Benzene
2	92	Toluene
3	106	Ethylbenzene or Xylene
4	104	Styrene
5	102	Phenylacetylene
6	120	Isopropyl benzene or Ethyl toluene
7	118	Isopropenyl benzene
8	118	Indan (2,3-Dihydroindene)
9	116	Indene
10	134	sec-Butyl benzene or isomer
11	132	Methylindan
12	132	Cinnamaldehyde or Vinyl benzaldehyde
13	130	Methylindene
14	128	Naphthalene
15	136	O-Phenylene cyclic carbonate
	146	Dimethylindan or Ethylindan
16	134	Methylacetophenone or Cymene
	144	2-Naphthol,3-Phenylfuran or 2-Vinyl benzofuran
17	142	Methylnaphthalene
18	94	Phenol
19	154	Biphenyl
	168	Methylbiphenyl
	170	Diphenyl ether
20	108	Cresol
	152	O-Vanillin
21	122	Ethylphenol
	166,168	Unidentified
	182	2-Ethylbiphenyl
	184	Phenyl-p-tolyl ether
22	136	Isopropyl phenol
	166	Unidentified
	182	Unidentified
	196, 198	Unidentified
23	150	Unidentified
	210, 212	Unidentified
24	228	Bisphenol A
	240	Unidentified
25	198?	Unidentified
	242	Unidentified
26	256	Unidentified
27	270	Unidentified
28	284	Unidentified

TABLE 25

COMBUSTION PRODUCTS OF POLYCARBONATE AT SEVERAL COMBUSTION CONDITIONS
(800 C maximum)

Air flow, cc/min	100	100	100	200
Oxygen flow, cc/min	0	0	20	0
Heating rate, C/min	5	50	5	5
Carbon dioxide*	960	985	1010	1100
Carbon monoxide	610	270	780	1125
Methane	12.2	39.8	14.3	17.8
Ethylene	0.82	1.28	0.99	1.07
Ethane	0.71	0.94	0.87	0.94
Propylene	0.31	0.50	0.39	0.33
Propane	0.67	0.15	0.15	0.15
Butane	0.20	0.19	0.91	0.11
Methanol	1.69	1.72	4.05	1.71
Acetaldehyde	1.03	0.86	1.83	0.96
Benzene	3.49	1.48	2.05	2.44
Toluene	1.16	0.47	0.83	1.18
%Plastic Accounted for	63	51	72	89
%Residue (by difference)	37	49	28	11

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 26

COMBUSTION PRODUCTS OF POLYCARBONATE AT SEVERAL COMBUSTION CONDITIONS
(1000 C maximum)

Air flow, cc/min	100	100	100
Oxygen flow, cc/min	0	40	0
Heating rate, C/min	5	5	50
Carbon dioxide*	1146 ± 157	747 ± 36	991 ± 34
Carbon monoxide	395 ± 36	425 ± 31	76 ± 12
Methane	27.2 ± 1.0	9.5 ± 1.6	25.9 ± 0.20
Ethylene	1.57 ± 0.27	1.31 ± 0.16	2.94 ± 1.67
Ethane	0.92 ± 0.08	0.80 ± 0.02	0.99 ± 0.11
Propylene	0.82 ± 0.33	0.56 ± 0.12	1.24 ± 0.81
Propane	0.23 ± 0.11	0.14 ± 0.04	0.25 ± 0.14
Methanol	1.48 ± 0.18	1.89 ± 0.32	1.07 ± 0.11
Acetaldehyde	0.72 ± 0.38	0.90 ± 0.41	0.58 ± 0.34
1-Butene	0.26 ± 0.12	0.20 ± 0.07	0.56 ± 0.38
Butane	0.08 ± 0.07	0.05 ± 0.05	0.09 ± 0.08
Benzene	1.97 ± 0.08	2.48 ± 0.69	3.75 ± 0.22
Toluene	1.10 ± 0.12	1.31 ± 0.22	3.33 ± 0.25
Ethylbenzene	0.67 ± 0.18	0.69 ± 0.03	1.90 ± 0.15
Styrene	0.10 ± 0.03	0.10 ± 0.01	0.31 ± 0.02
%Plastic accounted for	60	49	43
%Residue (by difference)	40	51	57

*The quantity of each combustion product is reported in milligrams per gram of sample.

explained in the Methodology section.

Quantities of products for the three polycarbonates tested using the 0-to 1000-C range were so similar that results were averaged (Table 26). Standard deviations were calculated which include in this case differences between the three plastics as well as experimental error and the randomness of the combustion process. One sample contained some filler material which contributed excess hydrocarbons, so the averages for some minor products are weighted toward that sample. Where deviations are larger than 25 percent, such as for propylene and butane, that sample is responsible. Carbon monoxide, carbon dioxide, and methane are the major volatile products. The latter two show significant decreases in the presence of excess oxygen. The faster heating rate allows most of the reaction with oxygen to occur at higher temperatures and thus favors production of carbon dioxide over carbon monoxide. The amounts of aliphatic hydrocarbons decrease with chain length. The unsaturated aliphatic compound is consistently present in greater amount than the corresponding saturated compound. Relatively small amounts of volatile aromatic hydrocarbons were detected. This may be due to the fact that the large amount of liquid residue consists of phenol and substituted phenols in which the lower-boiling aromatics are quite soluble. The percent plastic accounted for was calculated as the sum of the percents of the volatile products, assuming that carbon dioxide and carbon monoxide are formed from half of the 16 percent oxygen in polycarbonate and that the remainder of these compounds are formed by reaction of the carbon skeleton of the plastic with oxygen in the air. Volatile products, identified in quantities less than 2 milligrams per gram of sample but not otherwise quantitated, include methyl acetylene, acetone, isobutane, cis-2-butene, pentane, cyclopentene, and xylene.

Table 27 shows quantities of the combustion products of one polycarbonate sample observed within temperature ranges selected on the basis of the TGA curve. Totals for this sample are quite representative of the two unfilled polycarbonates. As expected carbon dioxide and carbon monoxide form primarily in the last stage, but also are significantly present in the first stage. This is the first tested plastic which formed these compounds at such low temperatures, indicating decomposition of the carbonate linkages. If all the oxygen of carbon dioxide and carbon monoxide in the first temperature range came from carbonate linkages, about half the oxygen of the plastic would be accounted for. Only the quantities of methane did not add up to a total expected from Table 26. The percent plastic accounted for is about the same. The lowest range is quite deficient in aliphatic hydrocarbons, but otherwise no trends are evident. Aromatic hydrocarbons are formed primarily at higher temperatures, that is, after the 520-C endotherm.

TABLE 27

POLYCARBONATE COMBUSTION PRODUCTS WITHIN SEVERAL TEMPERATURE RANGES

Compound	<475 C	475 - 500 C	500 - 550 C	550 - 1000 C	Total
Carbon dioxide*	90	60	133	997	1280
Carbon monoxide	10.3	14.6	60	248	333
Methane	2.25	2.48	5.69	3.75	14.2
Ethylene	0.09	0.31	0.39	0.33	1.12
Ethane	0.057	0.19	0.36	0.12	0.73
Propylene	0.095	0.17	0.085	0.026	0.37
Propane	0.022	0.067	0.03	----	0.12
Methanol	0.093	0.43	0.36	0.14	1.02
Acetaldehyde	0.092	0.10	0.06	0.085	0.34
1-Butene	0.062	0.038	0.008	0.042	0.15
Butane	0.001	0.004	0.001	0.004	0.01
Benzene	0.045	0.077	0.72	1.06	1.90
Toluene	0.066	0.19	0.46	0.18	0.90
Ethylbenzene	0.013	0.088	0.21	0.17	0.48
Styrene	0.006	0.008	0.014	0.036	0.06
%Plastic accounted for					59
%Residue (by difference)					41

*The quantity of each combustion product is reported in milligrams per gram of sample.

Discussion

Polycarbonate is typical of the polymers containing only carbon, hydrogen, and oxygen in that, on inefficient combustion, it undergoes random chain scissions to form a large amount of liquid. The phenolic compounds are expected but naphthalenes and indenes had not been previously reported and the mechanism of their formation is not completely understood.

POLYPHENYLENE OXIDE

Introduction

Polyphenylene oxide is a linear polymer, the formula of which is shown in Figure 46. It consists of 79.3 percent carbon, 7.5 percent hydrogen, and 13.2 percent oxygen. It is commercially provided in the pure form and in a modified form, both being self-extinguishing and non-dripping and having continuously usable temperature ranges extending to above 100 C.[21,37] Military, aircraft, and household uses for this plastic have been developed and promise to increase because of its good thermal, electrical, and mechanical properties. Preliminary studies on this plastic were done under a previous grant.[20]

Samples

Of the four commercial samples tested, sample 1 consists of polyphenylene oxide with a small amount of titanium dioxide whitener, and samples 2 through 4 are modified polyphenylene oxides with either carbon or glass fillers.

Results

Thermal analysis. Differential thermal analysis records of polyphenylene oxide, heated at 5 C/min in helium and in air atmospheres, are shown in Figure 47. In helium two endothermic peaks appear, one at 425 C and one at 460 C. In air the 460-C endothermic peak is preceded and followed by exothermic peaks which may represent a continuous exothermic reaction (oxidation of carbon) on which an endothermic reaction (depolymerization) is superimposed. This is consistent with the observation that the plastic begins to char at about 375 C. A thermogravimetric analysis record of the same plastic, heated at 5 C/minute in an air atmosphere, is shown in Figure 48. The major weight loss occurs in two steps. The first begins at about 375 C and continues to 450 C, accompanied by a 56-percent weight loss. This is followed by a transition and a 10-percent weight loss from 450 to 510 C. The second major step begins at about 510 C and accounts for combustion of the remaining 34 percent of the plastic. The temperature at which the plastic is completely combusted depends on the air supply. Correlating DTA and TGA results, the DTA endotherms must correspond to depolymerization, rather than melting, as they occur at temperatures where large weight losses have occurred. The 460-C endotherm corresponds to the end of the first step in the TGA curve. The TGA transition is not clearly defined in the DTA record but may be represented by a shoulder on the large exothermic peak. This large exothermic DTA peak corresponds to the second step of the TGA curve.

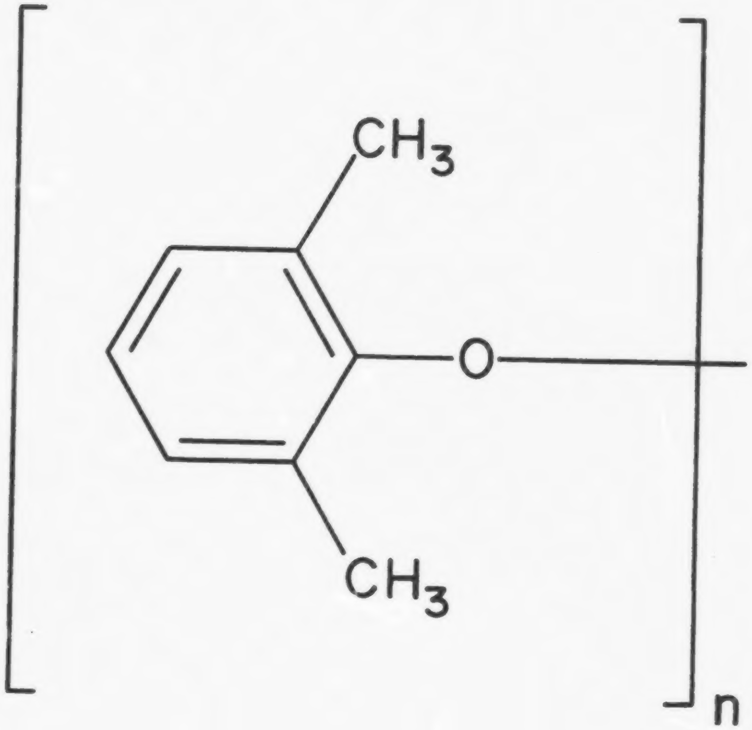


Figure 46. Poly-2,6-dimethyl-1,4-phenylene oxide

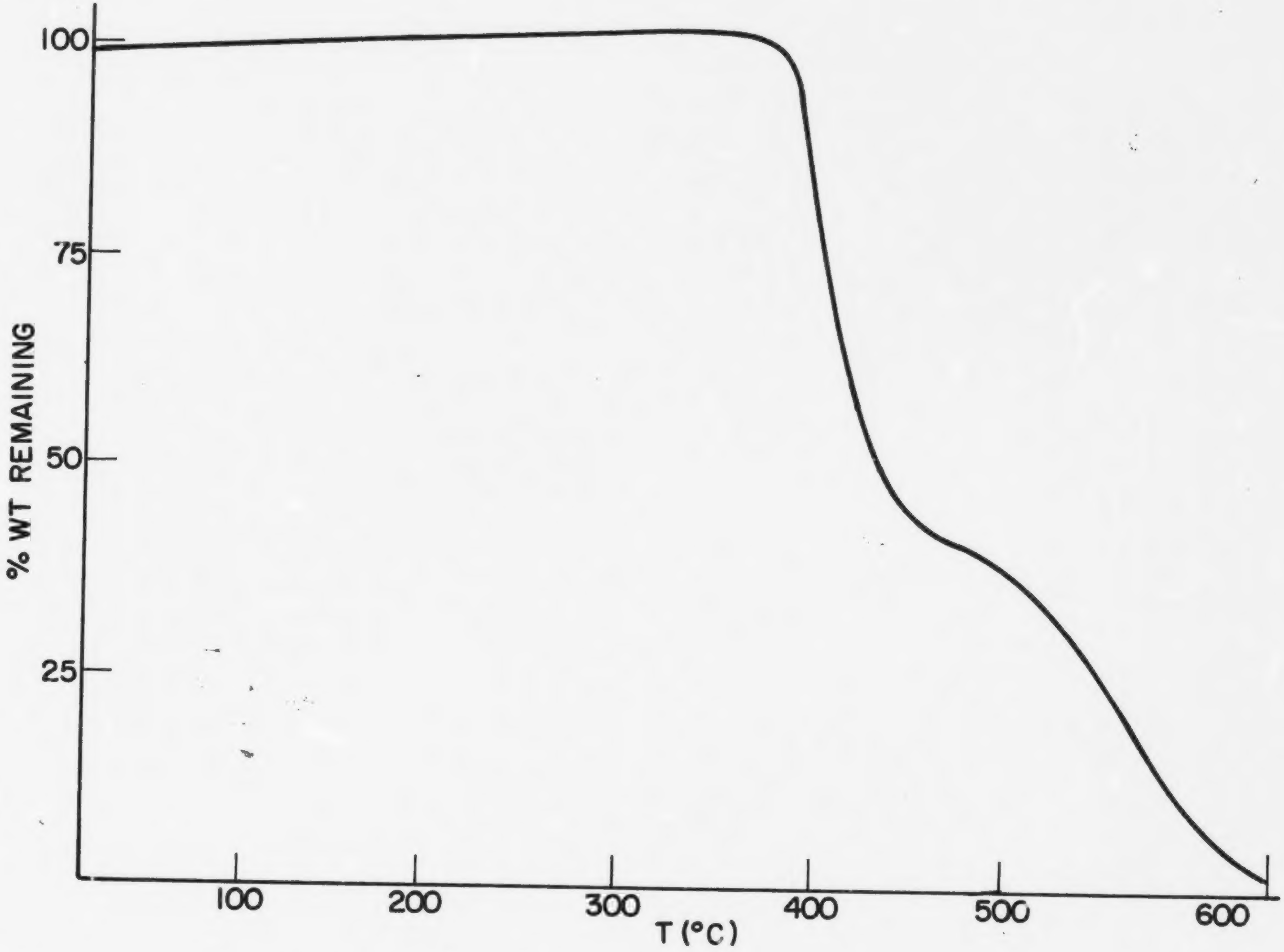


Figure 48. Thermogravimetric analysis record of polyphenylene oxide heated at 5 C/min in air

A similar situation exists for modified polyphenylene oxide as shown in Figures 49 and 50. In both oxidizing and inert atmospheres one significant endothermic peak occurs at 435 C and corresponds to the first step shown on the TGA record, a depolymerization with a 64-percent weight loss. Since the DTA records of modified polyphenylene oxide and polyphenylene oxide in helium were made using the same sample weights, a comparison indicates that depolymerization of modified polyphenylene oxide is more stongly endothermic. The shoulder on the large exothermic peak in Figure 49 could correspond to the TGA transition, while the large exothermic DTA peak above 500 C corresponds to the second step of the TGA curve.

The complexity of the combustion process makes interpretation of all features of the DTA and TGA records difficult. Major emphasis has been placed on interpreting those features of the DTA records involving generation of products, with little emphasis on determining melting, softening, or glass transition temperatures which may be found elsewhere.[38]

Qualitative analysis. Carbon dioxide, carbon monoxide, and methane were identified by infrared analysis of the combustion gas using a 10-cm path-length gas cell. Strong bands characteristic of aromatic compounds also appeared in the infrared spectrum. Further identifications were made by mass spectrometry after separation of individual products by gas chromatography.

Gaseous polyphenylene oxide combustion products separated on a six-foot-long, 1/4-in.-diameter column of Porapak Q include hydrocarbons through butane plus methanol and acetaldehyde (Figure 51). Figure 52 shows a chromatogram of gaseous polyphenylene oxide combustion products on a 12-foot-long, 1/4-in.-diameter column of 5 percent Squalane on Chromasorb P. A total of seventeen gaseous products were eluted in the same order as that presented in Table 29 beginning with methane and continuing through styrene. As can be seen from the attenuations indicated in Figure 52 aromatic compounds are present in substantially greater quantities than aliphatics. All four samples show the same qualitative picture except that samples 2 through 4 have a few additional small peaks. No attempt has been made to identify some of the smaller peaks in the Squalane chromatogram.

Between 400 C and 475 C, water and dense yellow-brown fumes are produced which condense in the combustion tube on leaving the heating zone. Much of the weight loss in the first step results from this condensate. Any of the remaining organic volatile material boils at too high a temperature to be eluted in a reasonable time chromatographically under column conditions used for the volatile products. Other investigators found that, in vacuum, products volatile at room temperature represent less than 4 percent of the total.[39]

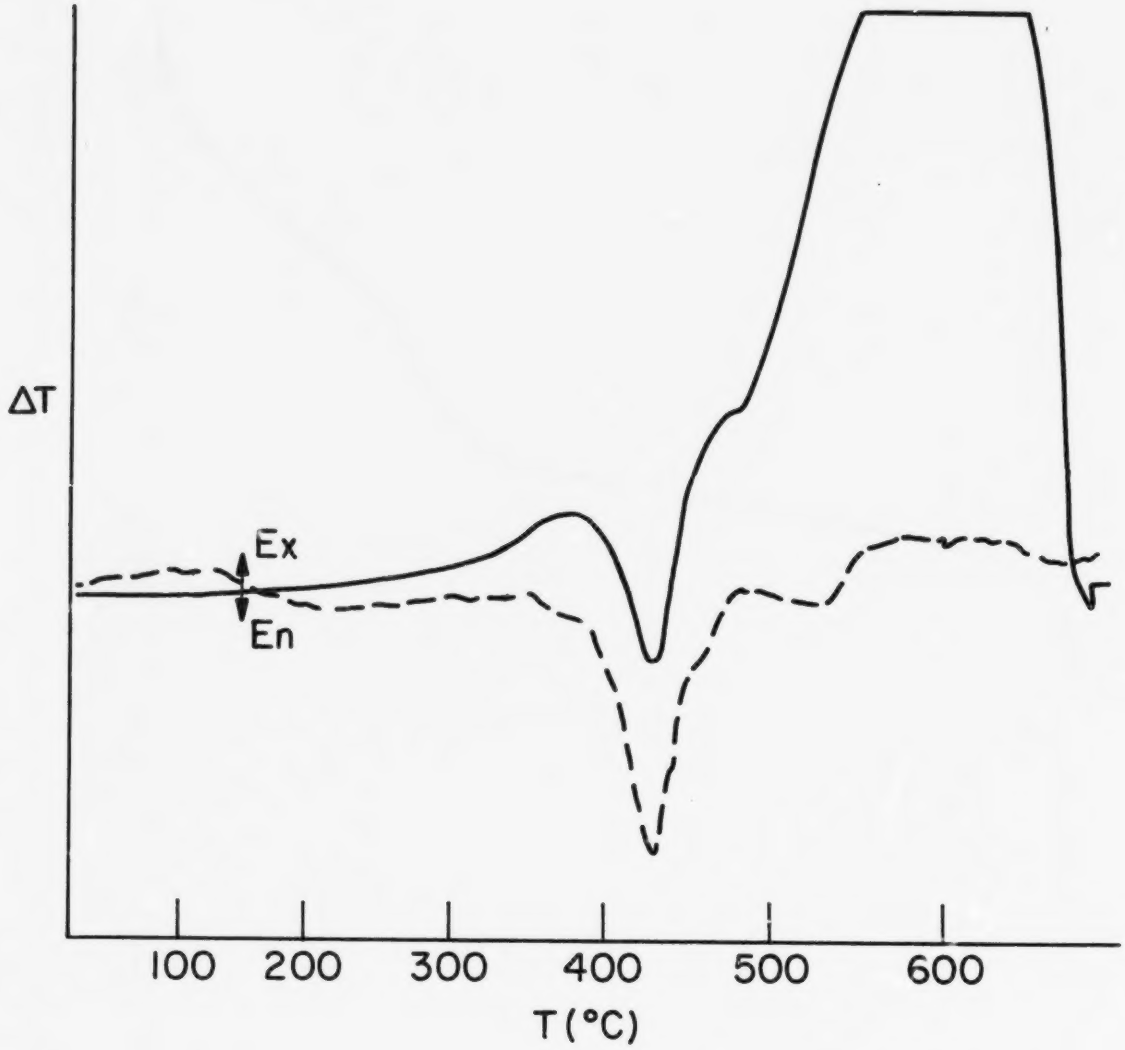


Figure 49. Differential thermal analysis records of modified polyphenylene oxide heated at 5 C/min in helium (broken curve) and air (smooth curve)

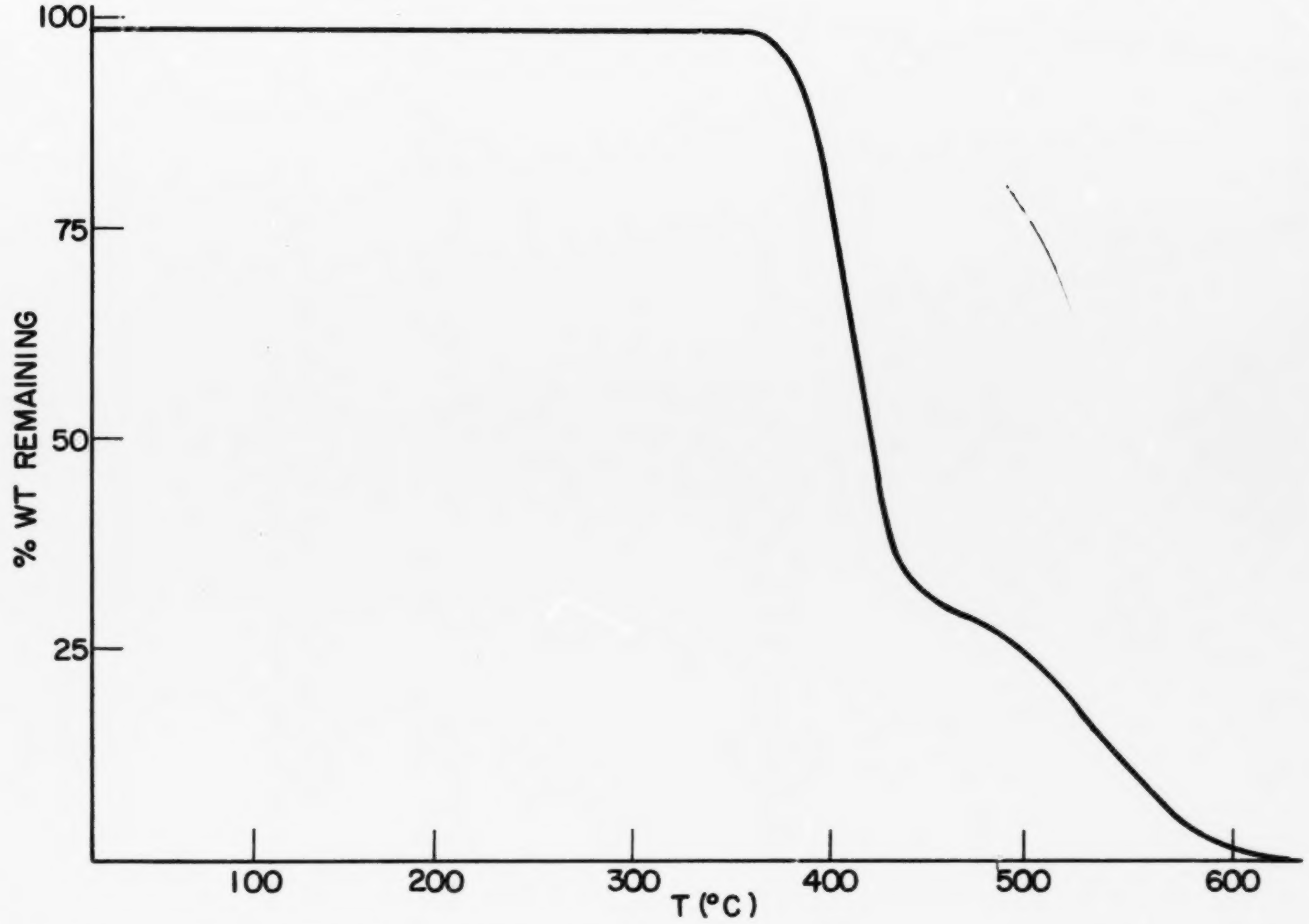


Figure 50. Thermogravimetric analysis record of modified polyphenylene oxide heated at 5 C/min in air

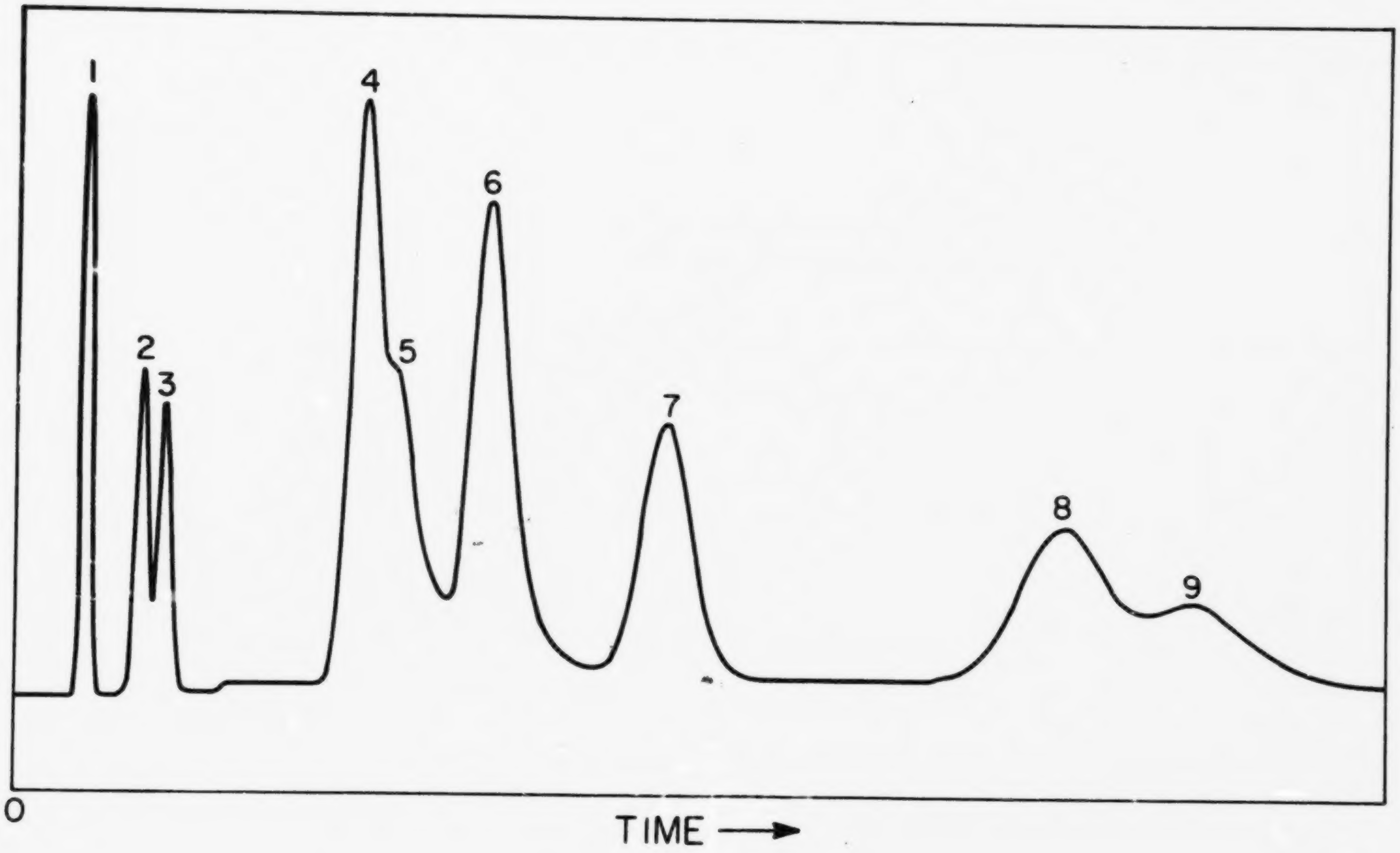


Figure 51. Chromatogram of polyphenylene oxide combustion products on a Porapak Q column

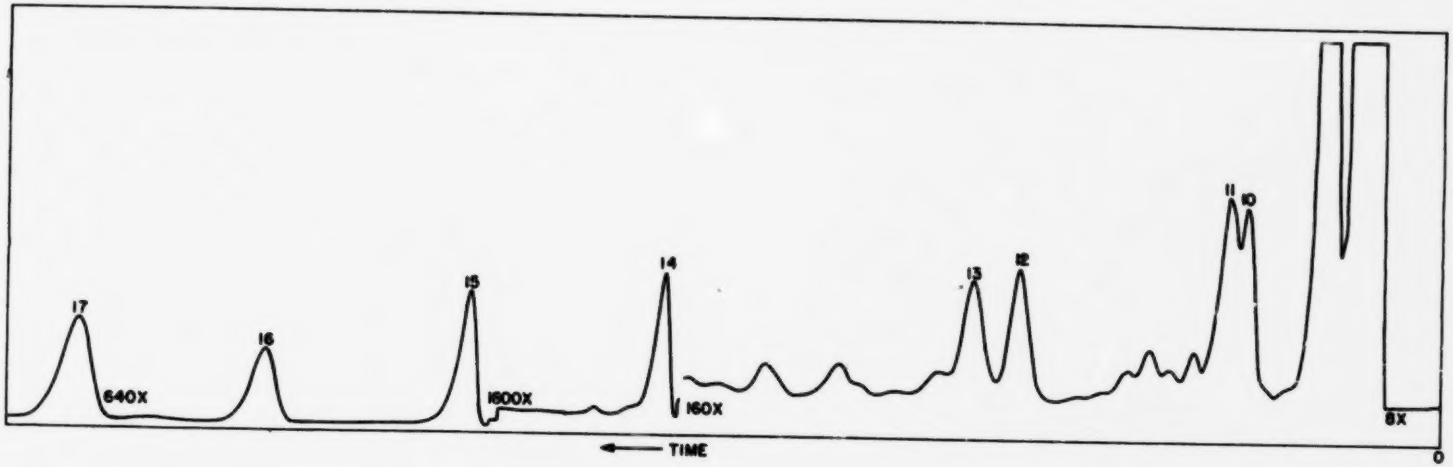


Figure 52. Chromatogram of polyphenylene oxide combustion products on a column of 5 percent squalane on Chromosorb P

Although the primary aim of this study was to analyze the volatile combustion products, it was decided to identify some components of the condensate because of their large amount, pungent odor, and indications from preliminary work that they could be toxicologically more significant than the identified volatile products. Infrared analysis of the condensate, after removal of water, indicates that it is a complex mixture of aromatic compounds. It includes small amounts of toluene, ethylbenzene, and styrene so that cited quantitative figures for these compounds must be accepted as minima.

The GC-MS 30 instrumentation with a 13-in.-long, 1/4-in.-diameter column of low K' Durapak was used to identify components of the liquid residue. About thirty peaks appeared in the chromatogram (Figure 53). The numbered peaks are characterized or identified in Table 28. Many peaks represent compounds present in small amounts. There are only four major peaks and these indicate the presence of 2, 6-xylenol, O-cresol, 2,4-xylenol and trimethylphenol. The isomers were determined by infrared spectroscopy, as mass spectra of isomers are nearly identical. Although no quantitative work was done on the liquid residue components, the quantities of the four major compounds are estimated to be ten to one hundred times as great as those of the other components of the condensate.

Quantitative analysis. Table 29 shows quantities of identified gaseous products from each of the four samples run using a temperature programming rate of 5 C/min from 350 to 800 C after initial rapid heating to 350 C. There was sufficient air, when integrated over the entire run, to convert all the carbon to carbon dioxide, as explained in the Methodology section. Actually there was a slightly deficient oxygen condition. All results are given in milligrams per gram of plastic. Carbon dioxide and carbon monoxide, as expected, are the major volatile combustion products. Although the ratio of the two compounds varies considerably, significant amounts of carbon monoxide are produced by all the samples. Straight-chain saturated and unsaturated hydrocarbons, except methane, are present in trace amounts, with an unsaturated compound occurring at about twice the concentration of the corresponding saturate. The three substituted aromatic compounds rank with methane as the principal volatile hydrocarbon constituents of the combustion products. Residue represents only inert material remaining in the combustion boat after a run and does not include volatile products which condense in the end of the combustion tube or in the collection bag. It can be seen that Sample 1, the unmodified polyphenylene oxide, differs slightly from the other samples, which are modified polyphenylene oxides. Samples 2 and 3 show nearly identical products and differ from Sample 4, which forms a large amount of inorganic residue. Volatile products listed in Table 29 account for about 50 percent of the weight of each polymer combusted. Water (vapor and liquid), which was not quantitated, and high-

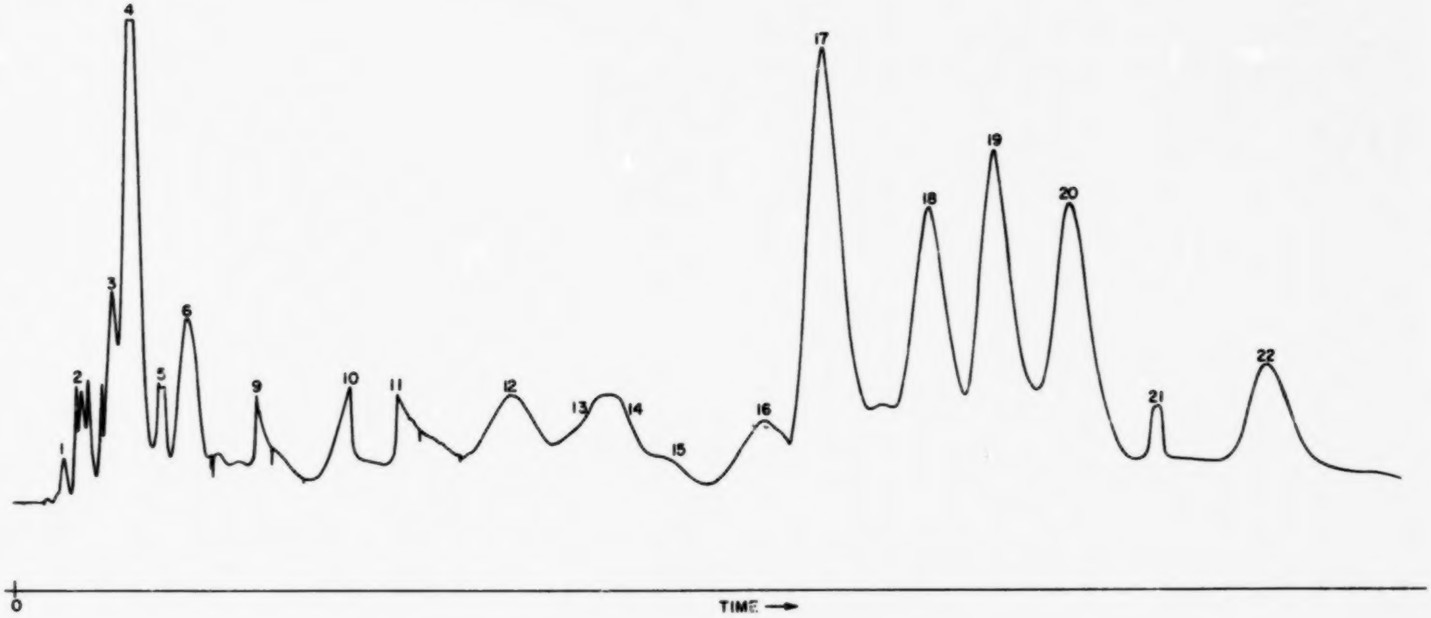


Figure 53. Chromatogram of polyphenylene oxide liquid residue on a low K' Durapak column

boiling organic compounds account for the remainder of the plastic.

TABLE 28

IDENTIFICATION OF POLYPHENYLENE OXIDE RESIDUE CHROMATOGRAM PEAKS

Peak Number	Molecular Weight	Identification
1	78	Benzene
2	92	Toluene
3	106	Ethylbenzene or Xylene
4	104	Styrene
5	120	Trimethylbenzene*
6	118	Indan
7	116	Indene
8	---	Unidentified
9	---	Unidentified
10	132	Phenyl propynyl ether*
11	134	o-Cymene*
	128	Naphthalene
12	136	o-Cresyl ethyl ether*
13	146	Dimethylindan
14	150	Unidentified
15	---	Unidentified
16	142	Methylnaphthalene
17	122	2,6-Dimethylphenol
18	108	o-Cresol
19	136	Trimethylphenol
20	122	2,4-Dimethylphenol
	166	2-(x-Xylyloxy) ethanol?
21	136	Trimethylphenol
22	196	Unidentified

*Or isomer.

Sample 1 was employed to test the effect of combustion conditions on amounts of products generated. Several runs were made using the 5-C/min heating rate and varying amounts of air. The first air supply was about half that required to convert all the carbon of the plastic to carbon dioxide. The second air supply, when integrated over the entire run, was just sufficient to convert all the carbon to carbon dioxide. The addition of pure oxygen to the third air supply provided an excess. Results are shown in Table 30. The run with deficient oxygen shows the least amount of carbon monoxide. This is explained by the fact that the plastic requires about a one-half-hour exposure at 800 C, the maximum temperature of our apparatus, to combust completely in this air

TABLE 29

QUANTITIES OF COMBUSTION PRODUCTS FROM SEVERAL POLYPHENYLENE OXIDE PLASTICS

Product	Sample 1	Sample 2	Sample 3	Sample 4
Carbon dioxide*	838.	503.	572.	337.
Carbon monoxide	457.	425.	377.	330.
Methane	18.2	9.09	9.63	5.33
Ethylene	0.58	1.27	1.01	0.54
Ethane	0.80	0.65	0.64	0.39
Propylene	0.30	0.50	0.40	0.17
Propane	0.22	0.26	0.24	0.11
Methanol	1.52	1.60	1.46	0.97
Acetaldehyde	1.13	1.77	1.34	0.98
1-Butene	0.29	0.66	0.57	0.20
Butane	0.17	0.24	0.23	0.08
1-Pentene	0.29	0.33	0.27	0.07
Pentane and pentadiene	0.32	0.31	0.27	0.08
Hexane	0.09	0.10	0.09	0.02
1-Hexene	0.22	0.29	0.23	0.04
Benzene	1.76	3.38	3.17	2.14
Toluene	22.9	34.6	34.8	27.8
Ethylbenzene	12.4	22.9	25.3	16.2
Styrene	21.5	72.0	64.8	57.4
Residue	14.0	3.0	1.0	260.0
%Plastic accounted for	52	47	46	61

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 30

VARIATION OF POLYPHENYLENE OXIDE COMBUSTION PRODUCTS WITH AIR SUPPLY

Product	Deficient O_2	Sufficient O_2	Excess O_2
Carbon dioxide*	887.0	838.0	830.0
Carbon monoxide	325.0	457.0	452.0
Methane	20.8	18.2	16.5
Ethylene	0.99	0.58	0.80
Ethane	0.82	0.80	0.68
Propylene	0.40	0.30	0.35
Propane	0.23	0.22	0.19
Methanol	1.68	1.52	2.65
Acetaldehyde	0.97	1.13	1.87
1-Butene	0.35	0.29	0.31
Butane	0.15	0.17	0.18
1-Pentene	0.27	0.29	0.18
Pentane and pentadiene	0.25	0.32	0.22
1-Hexene	0.29	0.22	0.19
Hexane	0.09	0.09	0.06
Benzene	2.76	1.76	2.29
Toluene	23.3	22.9	21.3
Ethylbenzene	10.4	12.4	10.7
Styrene	18.3	21.5	15.3

*The quantity of each combustion product is reported in milligrams per gram of sample.

supply. Since the amount of oxygen at any given time is less, the time required for combustion is much longer. Using the other two air supplies, the plastic is combusted at or before 800 C. It is significant that the amount of carbon monoxide generated seems to remain constant above a certain air supply. Minor fluctuations are observed in the other products, but they are so small that it cannot be determined whether they represent real trends, experimental error, or the normal deviations to be expected in the combustion process.

Table 31 shows the influence of heating rate on amounts of products generated. Using the sufficient airflow in each of the runs, the plastic was heated at the indicated temperature rate to 800 C. The study using the faster heating rate involved longer 800-C exposure before combustion was complete and favored the production of carbon dioxide rather than carbon monoxide. It is characteristic of the unsaturated-saturated aliphatic pairs that the unsaturated compound increases two to threefold at the higher heating rate, while the corresponding saturated compound remains about the same. Again, other trends are of a very minor nature.

Table 32 shows the quantities of the products produced in four temperature ranges selected on the basis of the TGA curve. The 5-C/minute heating rate and sufficient air supply were used. The first two temperature ranges cover the first step of the breakdown process, the third range covers the transition, and the last range covers the second step. As expected, carbon dioxide and carbon monoxide are mainly produced at higher temperatures, and their amounts account for nearly all the weight loss in the second step of the TGA curve. Aliphatic hydrocarbons except methane peak during the third temperature range. Aromatic hydrocarbons show no real trend as benzene peaks in the last range, toluene in the second, and ethylbenzene is about equally divided among the last three ranges. The amounts of volatile products from the first three temperature ranges should account for 0.6 gram of plastic, as indicated by the 60 percent weight loss on the TGA record. Considerably less of the plastic is actually accounted for by these products due to the generation of liquid residue.

Discussion

It is evident that, of the volatile combustion products identified, carbon monoxide presents the only significant health hazard. The substituted phenols identified in the condensate are all irritants and have significant vapor pressures at room temperature. Any contribution of the condensate to the overall toxicity of the combustion products could best be evaluated from animal exposure data.

TABLE 31

EFFECT OF HEATING RATE ON COMBUSTION PRODUCTS OF POLYPHENYLENE OXIDE

Product	5 C/min	50 C/min
Carbon dioxide*	838.0	908.0
Carbon monoxide	457.0	179.0
Methane	18.2	22.3
Ethylene	0.58	1.77
Ethane	0.80	0.76
Propylene	0.30	0.86
Propane	0.22	0.26
Methanol	1.52	0.94
Acetaldehyde	1.13	0.97
1-Butene	0.29	0.67
Butane	0.17	0.22
1-Pentene	0.29	0.51
Pentane and pentadiene	0.32	0.44
1-Hexene	0.22	0.64
Hexane	0.09	0.10
Benzene	1.76	3.03
Toluene	22.9	17.6
Ethylbenzene	12.4	7.07
Styrene	21.5	21.4

*The quantity of each combustion product is reported in milligrams per gram of sample.

TABLE 32

VARIATION OF POLYPHENYLENE OXIDE COMBUSTION PRODUCTS WITH TEMPERATURE

Product	350 - 400 C	400 - 450 C	450 - 510 C	510 - 800 C
Carbon dioxide*	3.6	23.8	89.7	780.0
Carbon monoxide	8.5	23.3	65.5	340.0
Methane	0.057	1.16	5.85	11.7
Ethylene	0.017	0.11	0.31	0.27
Ethane	0.041	0.14	0.46	0.18
Propylene	0.008	0.10	0.24	0.04
Propane	0.008	0.08	0.17	0.01
Methanol	0.015	0.51	1.23	0.31
Acetaldehyde	0.54	0.30	0.35	0.01
1-Butene	0.053	0.11	0.15	0.03
Butane	0.016	0.09	0.11	0.01
1-Pentene	0.008	0.09	0.17	0.02
Pentane and pentadiene	0.013	0.09	0.15	----
1-Hexene	0.008	0.07	0.17	0.03
Hexane	0.005	0.03	0.06	----
Benzene	0.087	0.37	0.43	0.79
Toluene	1.02	14.6	6.06	3.18
Ethylbenzene	0.27	3.77	3.47	3.89
Styrene	2.14	4.86	3.93	14.1

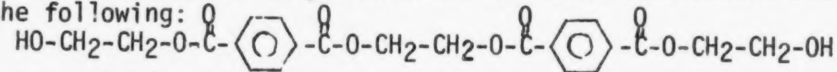
*The quantity of each combustion product is reported in milligrams per gram of sample.

POLYESTER

Several polyester film samples were sent to us by a county governmental agency which was responsible for disposal of large quantities of this material received at a landfill operation from a manufacturer in the area. Occasionally this film was received in such large quantities that it could not be buried and was disposed of by open burning. At this time landfill operators complained of eye and skin irritation and complaints of a strong odor in the air were received from up to ten miles away.

Thermal analysis was not performed on these samples. When heated at 5 C/min in the combustion furnace, the clear film melted down to a pale yellow mass at about 200 C, and turned brown between 250 and 300 C. At 350 C it began bubbling and giving off a white fume which condensed in the combustion tube and bag. The plastic was completely combusted by 500 C.

By far the largest portion of the slowly heated polyester film formed the white fume which condensed as a fine white powder. An emission spectrum of the powder revealed no metallic elements, indicating the powder to be organic rather than an inorganic in nature. A mass spectrum of the powder taken using the solid probe indicated a molecular weight of about 450 with a structure similar to the following:



$$HO\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}C_6H_4\text{-}\overset{O}{\overset{\|}{C}}\text{-}O\text{-}CH_2\text{-}CH_2\text{-}OH$$

This is probably a depolymerization product. Madorsky has done a more through analysis of similar residues.[5]

If some of the alcohol groups were replaced by aldehyde groups, the above compound could produce irritation. However, no white fume was noticed during the open burning so our attention was turned to gaseous products. Infrared analysis of the combustion gas showed bands due to carbon dioxide, carbon monoxide, methanol, and acetaldehyde. Methane, ethane, and benzene were also identified by mass spectrometry after separation on either a Porapak Q or Carbowax 20 M column. These were the only gaseous products identified. Acetaldehyde is the only compound identified which could cause the irritation and odor produced. Using the 5-C/min heating rate and 100-cc/min air flow, approximately 0.1 milligrams of acetaldehyde were found per gram of sample. However, this was probably much more efficient combustion than open burning of a bulky sample and it is possible that larger quantities of acetaldehyde could be produced.

This problem is typical of the disposal problems encountered with bulky products in both incineration and open burning.

SYNTHETIC FABRICS (DACRON^R, ORLON^R, NYLON)

The Flammable Fabrics Act includes a statement expressing the need to know the nature and toxicity of the combustion products of fabrics, and yet the importance of this information seems to be delegated to a secondary role. This is probably as it should be in considering the flammability of clothing. However, now that the act has been extended to household and interior furnishings, more attention should be given to this matter of the products of combustion because our environment is rapidly changing from an "open" to a "closed" nature. A few years ago we made provisions for opening the windows of our homes and other buildings to enjoy the fresh air. Now we go to increasingly greater efforts to seal buildings to keep out the polluted air or air of the wrong temperature. Likewise, in our modes of travel, for example, air conditioned motor vehicles, aircraft flying at altitudes requiring pressurization, and spacecraft traveling outside the atmosphere, we require a tightly closed environment. In these situations, a minor fire may not cause heat or burn damage to the occupant, but can easily cause oxygen depletion, or the generation of toxic and poisonous gases. We have already had examples in air travel where passengers have survived an air crash and the resulting fire, only to be killed by carbon monoxide and other products generated by the fire.

Analysis of combustion products of fabrics was not within the scope of the present grant and only preliminary thermal analyses have been carried out.

Results

Thermal analysis. A differential thermal analysis record of Dacron^R (Figure 54) shows a small endothermic peak at 260 C followed by a large exothermic peak between 430 and 530 C. Thermogravimetric analysis of the same sample (Figure 55) shows a two-step degradation, the first step beginning about 330 C and ending at 410 C, corresponding to an 85-percent weight loss. The remaining 15 percent of the sample is lost in an irregular fashion until the plastic is completely combusted at about 500 C. Little interpretation can be made of these records without some idea of products generated, although it is likely that the DTA endotherm corresponds to melting of the polymer and the DTA exotherm corresponds to the major weight-loss of the sample. Combustion under the TGA conditions seems to occur at slightly lower temperatures than at the DTA conditions.

A similar situation exists for Orlon^R (Figure 56 and 57). There is again a small DTA endotherm at 260 C and a large exothermic peak between 390 and 525 C. The TGA record is parallel to that of

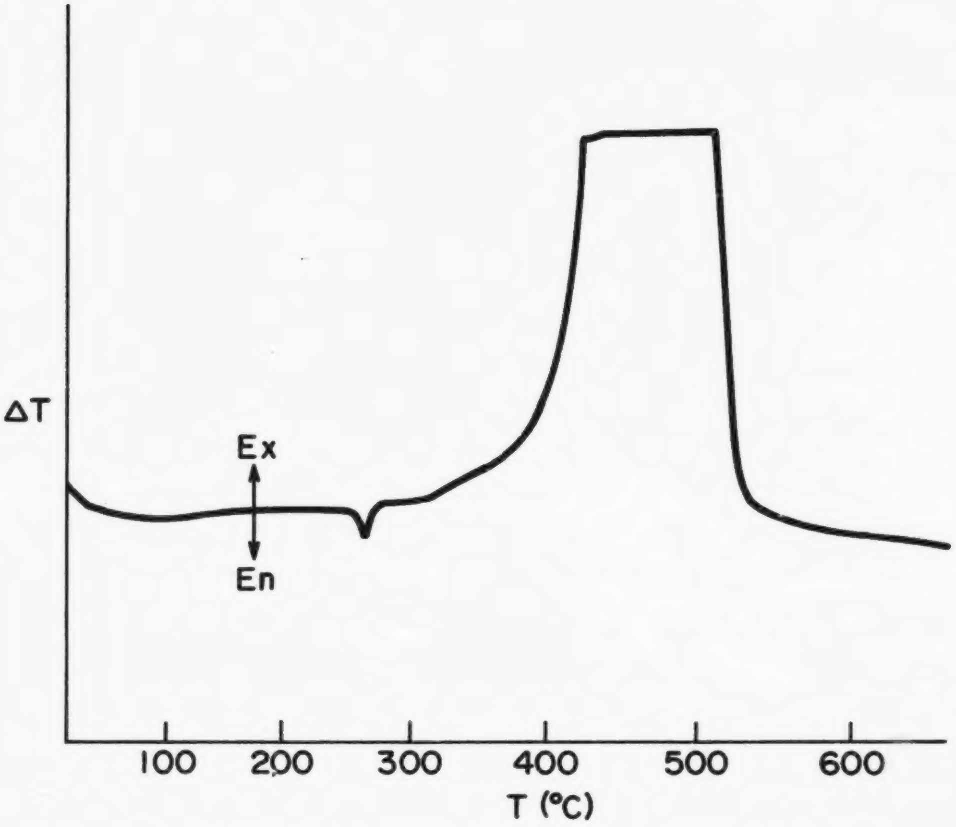


Figure 54. Differential thermal analysis record of Dacron^R heated at 5 C/min in air

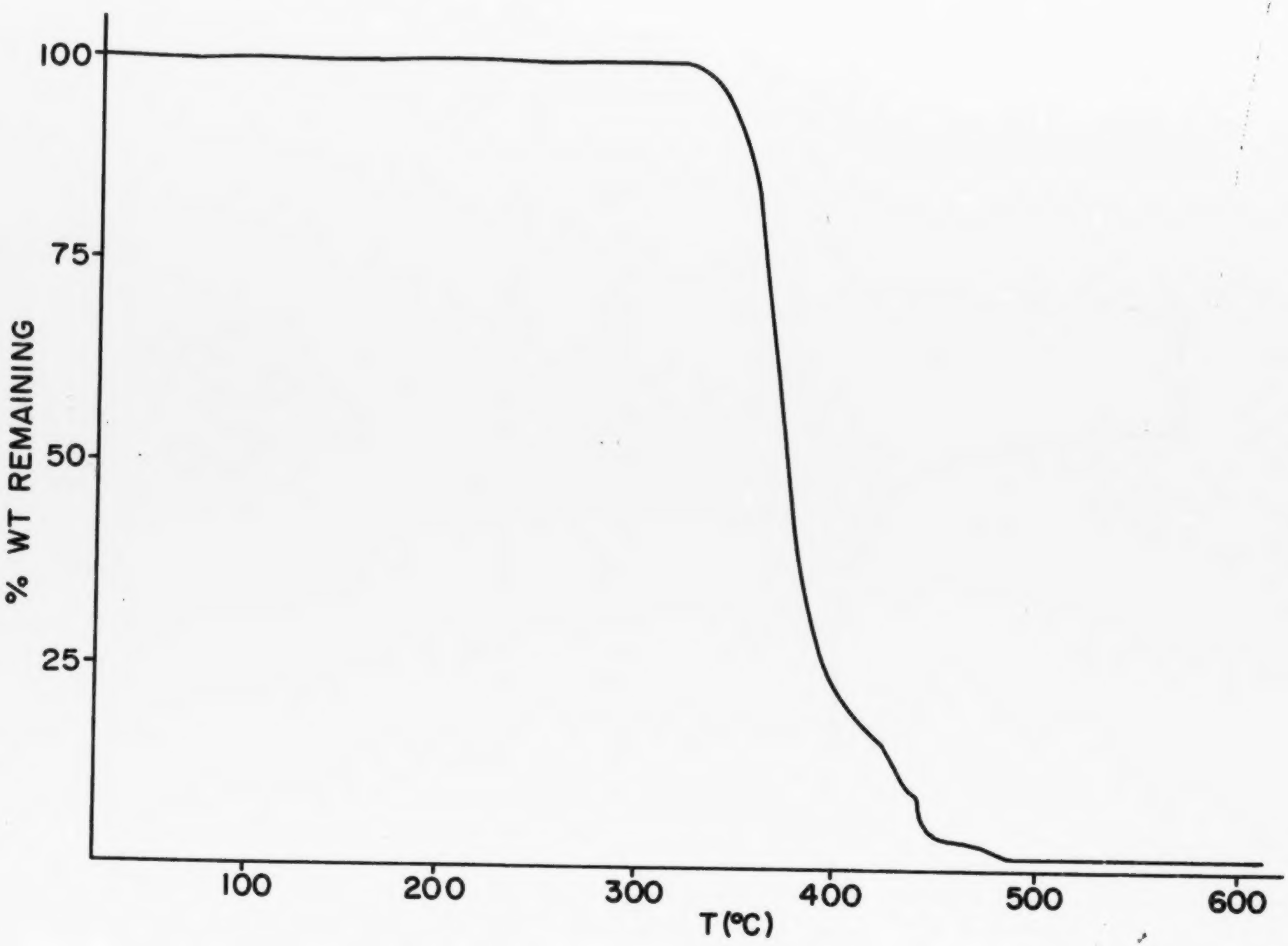


Figure 55. Thermogravimetric analysis record of Dacron^R heated at 10 C/min in air

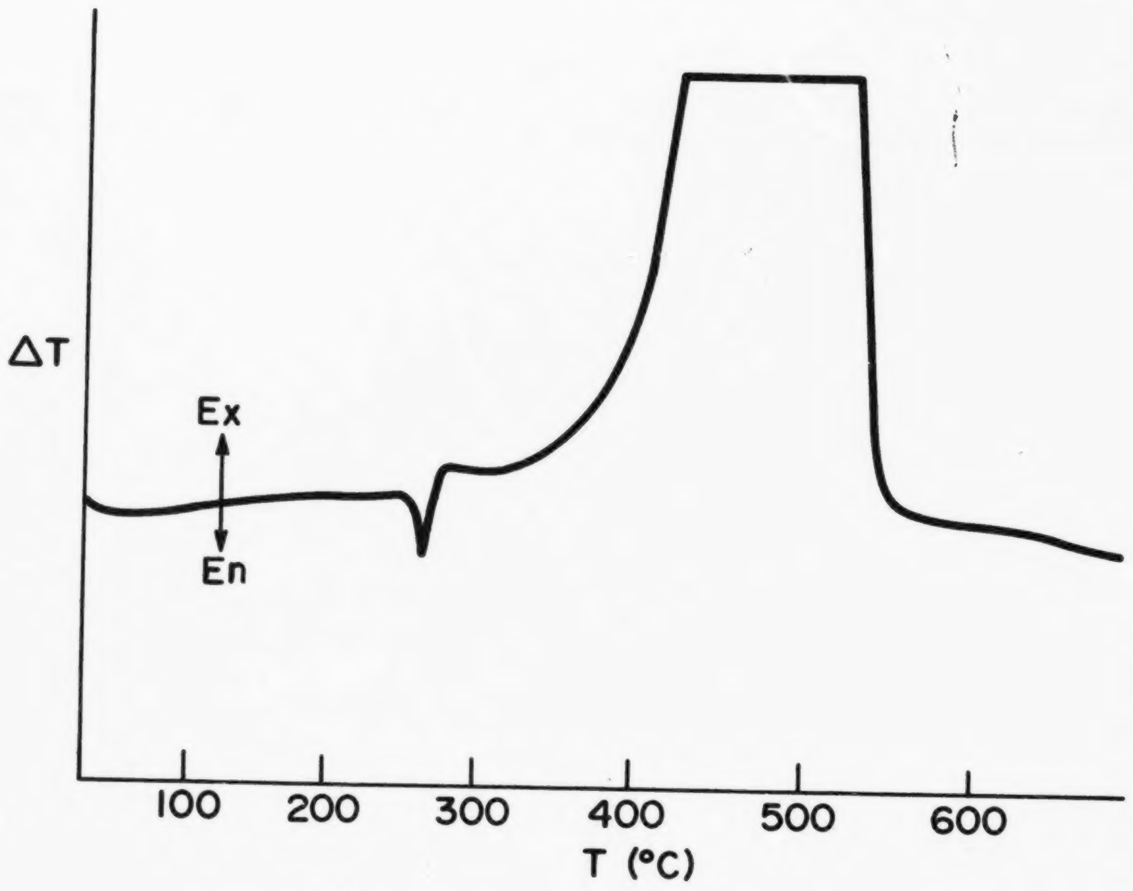


Figure 56. Differential thermal analysis record of Orlon^R heated at 5 C/min in air

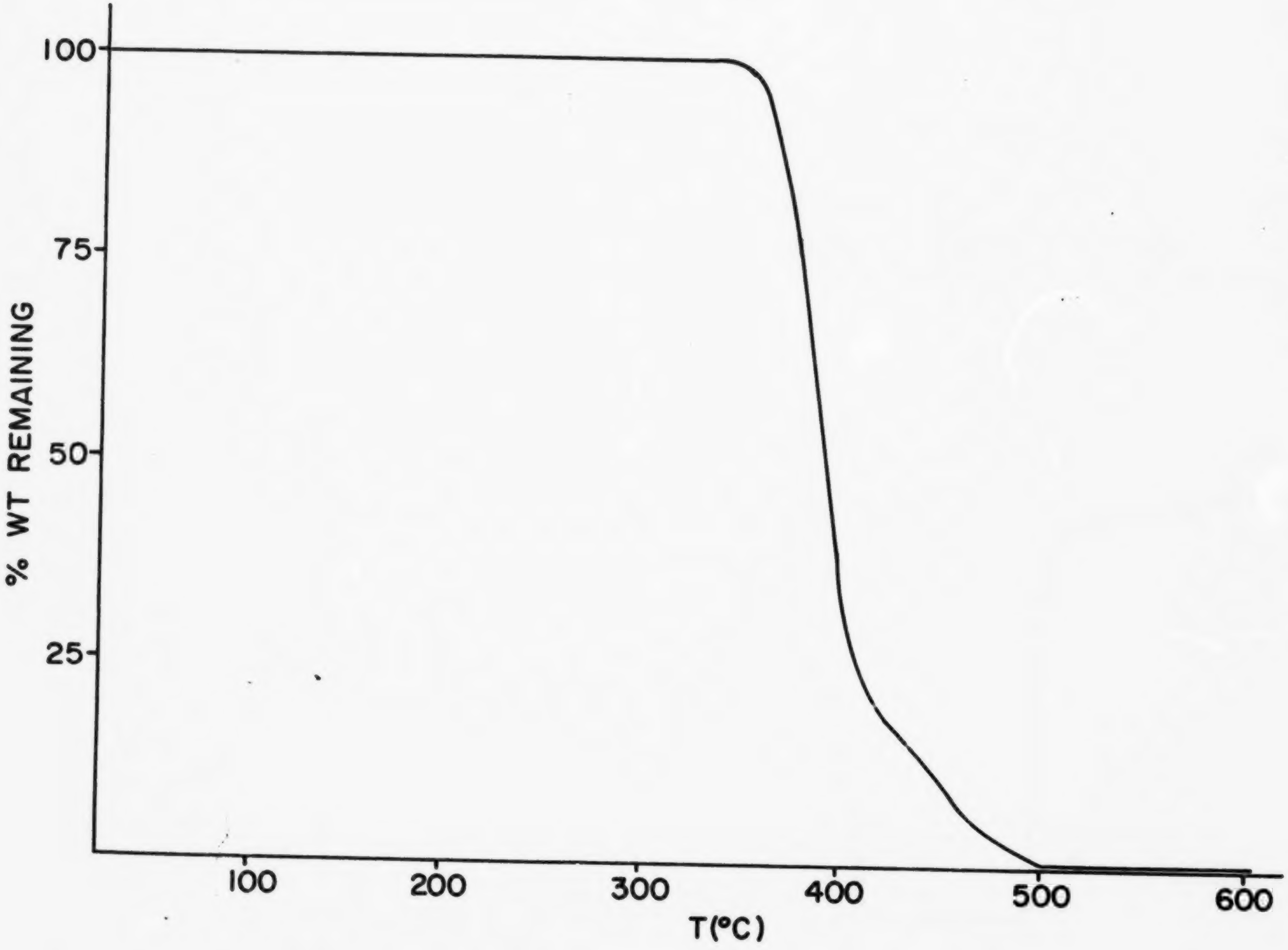


Figure 57. Thermogravimetric analysis record of Orlon^{R} heated at 10 C/min in air

Dacron^R but is displaced about 10 C higher in temperature.

Nylon is similar to the other fabrics except that its DTA record has an additional small exothermic peak at about 350 C and its TGA record is displaced 10 C higher than Orlon^R in temperature (Figures 58 and 59).

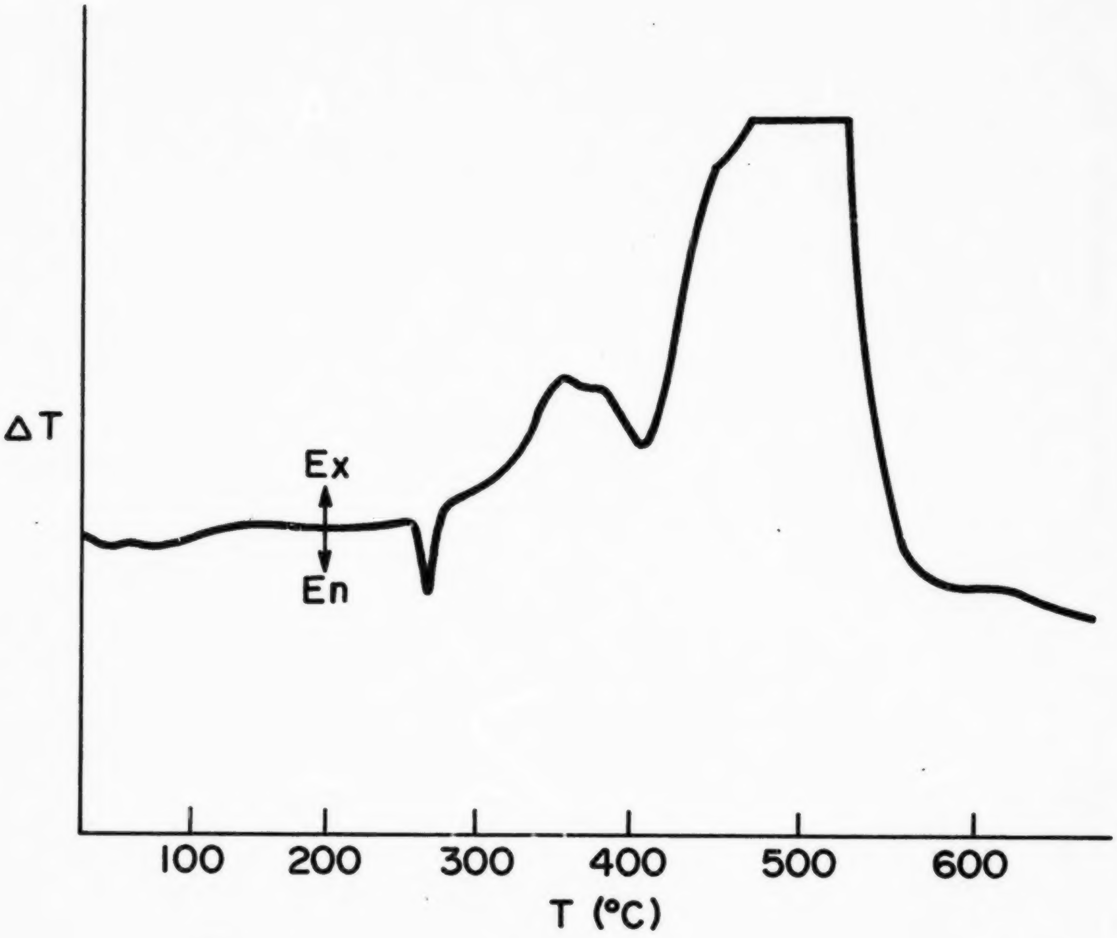


Figure 58. Differential thermal analysis record of nylon heated at 5 C/min in air

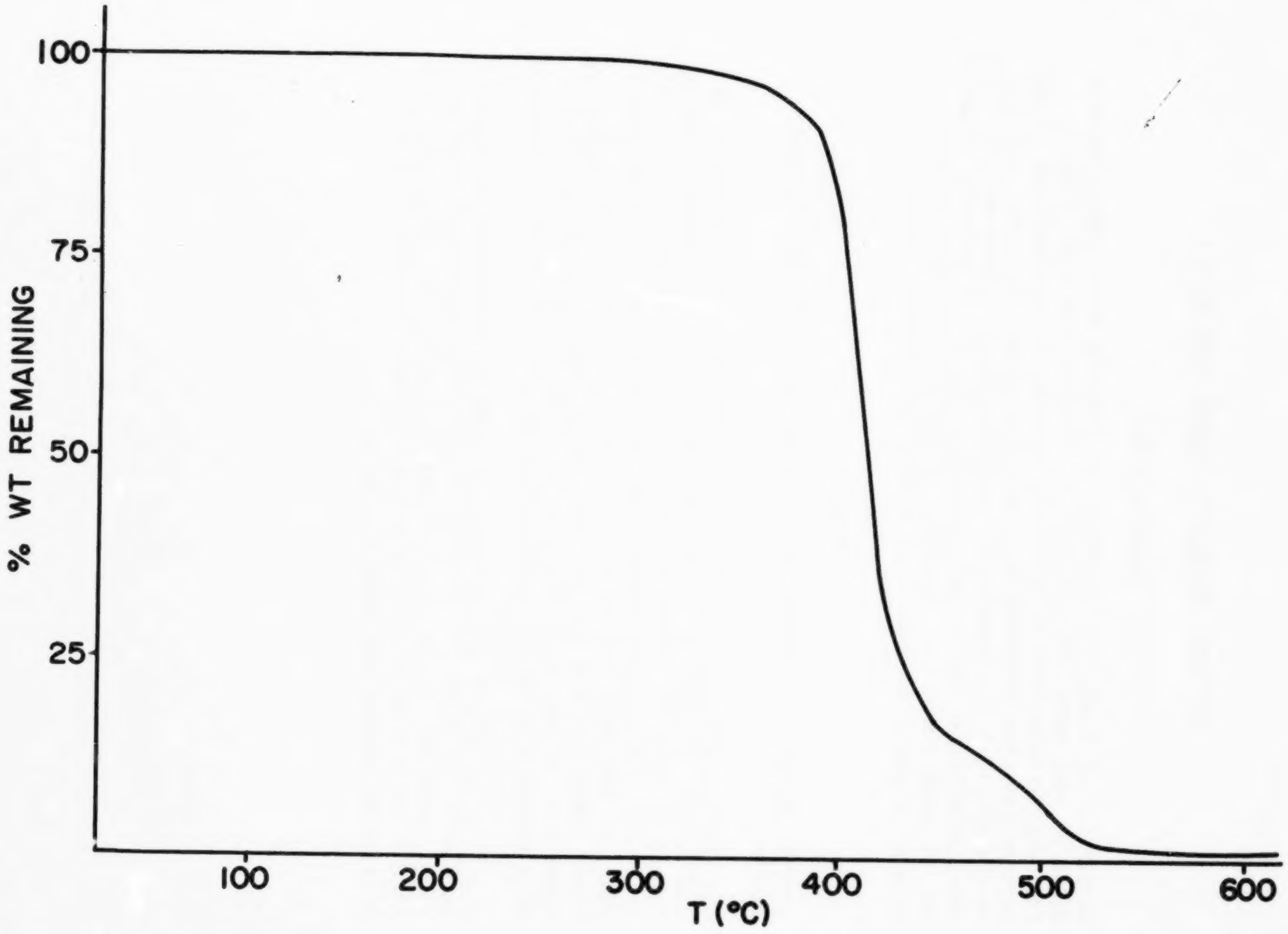


Figure 59. Thermogravimetric analysis record of nylon heated at 10 C/min in air

NATURAL PRODUCTS (WOOD AND WOOL)

Introduction

Comparison of combustion products of plastics with combustion products of some materials replaced by plastics and with commonly-incinerated materials is desirable in order to maintain the proper perspective when interpreting combustion data. We chose wood and wool with which to compare the carbon-hydrogen-oxygen-and the nitrogen-containing polymers, respectively. Our first priority, however, was to study combustion products of plastics and work on these natural products to date is of a very preliminary nature.

Results

Thermal analysis. Thermal analysis was not performed on these samples.

Qualitative analysis. GC-MS analysis of the gaseous products of combustion of wood on a five-foot-long, 1/4-in.-diameter Porapak Q column (Figure 60) showed thirteen peaks in addition to air. Fifteen mass spectra were taken (sometimes more than one spectrum per peak, as numbered) and identifications are listed in Table 33. Other compounds have not yet been identified. Gaseous products of combustion of wool were analyzed by infrared spectroscopy, but only carbon dioxide and carbon monoxide were positively identified.

Quantitative analysis. Analysis of wood (0.14 percent nitrogen) combustion products for cyanide ion at three combustion conditions (100-cc/min air, 5-and 50-C/min heating rates; and 100-cc/min air plus 20-cc/min oxygen, 5-C/min heating rate) resulted in 0.3-0.4 milligrams cyanide per gram of sample.

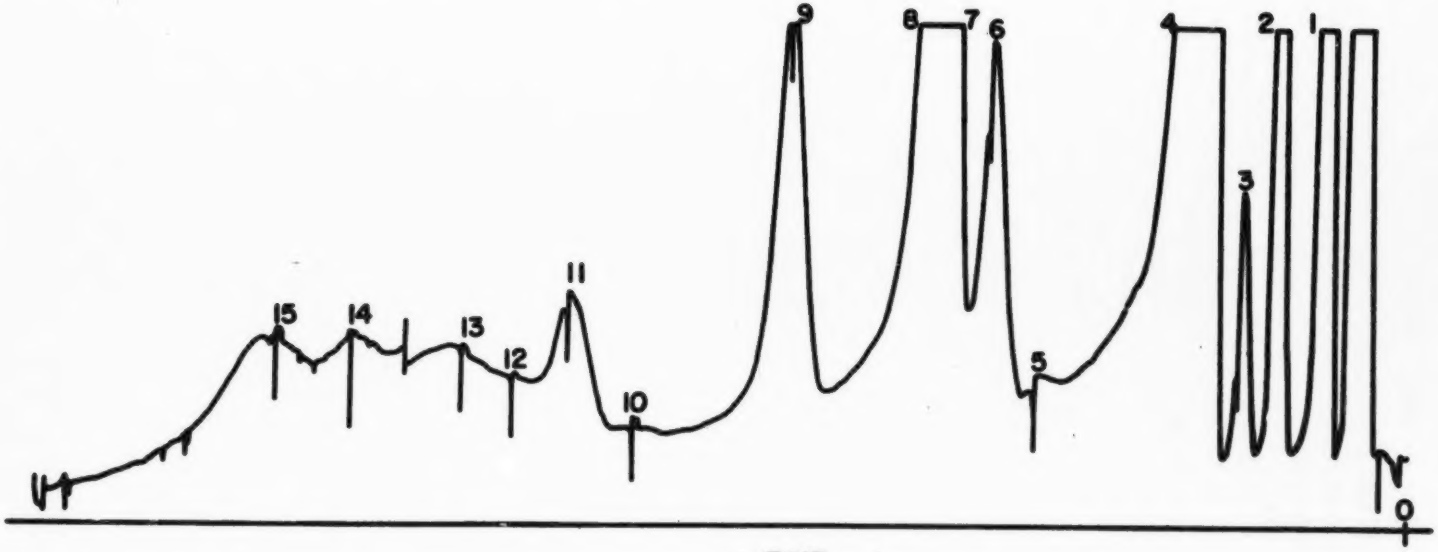


Figure 60. Chromatogram of wood combustion products on a Porapak Q column

TABLE 33

IDENTIFICATION OF WOOD CHROMATOGRAM PEAKS

Scan Number	Molecular Weight	Identification
1	44	Carbon dioxide
2	28	Ethylene
3	30	Ethane
4	18	Water
5	--	Unidentified
6	42	Propylene
7	32	Methanol
	44	Propane
8	32	Methanol
	50	1,3-Butadiyne?
	52	1-Buten-3-yne?
9	44	Acetaldehyde
10	60	n-Propanol
11	54	Butadiene
	56	Butene or Isobutene
12,13	56	Butene (Isomer?)
14	56	Butene (Isomer?)
15	58	Butane
	68	Pentadiene

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Second, we are indebted to those manufacturers who furnished us samples, generally displaying an interest in the work, and sometimes indicating some trepidation in turning over data concerning their samples, but still doing so. We appreciate the interest shown us in our work by M. O'Mara, L. Crider, and W. E. McCormick of the Goodrich Tire and Rubber Company, and thank them for the many plastic samples furnished us. Likewise we are grateful to all sample suppliers, including the Uniloy Division of the Hoover Ball & Bearing Company, General Electric Company, E. I. DuPont de Nemours and Company, Olin Research Center, Monsanto Company, Union Carbide & Chemical, Scott Paper Company, Mobil Chemical Company, and Firestone Plastics Company.

Lastly, we are indebted to Louis Lefke, Dan Keller, Alvin Keene, and E. Timothy Oppelt, formerly with the Solid Wastes Research Laboratory of the U. S. Environmental Protection Agency. Especially helpful in the latter phases of the program was Nancy Ulmer, Project Officer, Solid Wastes Research Laboratory.

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